Minnesota Wild Rice Sulfate Standard 2013 Field Survey - Quality Assurance Project Plan

August 2013

Minnesota Pollution Control Agency
520 Lafayette Road North
St. Paul, Minnesota 55155-4194

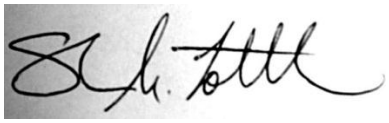
Minnesota Pollution Control Agency

Section A: Project Management Elements

Section A.1: Approvals

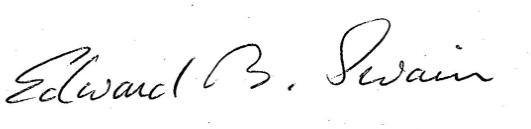
Approval: Date:

Amy Myrbo, PhD
University of Minnesota – Twin Cities (UMN)
National Lacustrine Core Facility/Limnological Research Center (LacCore/LRC)
Principle Investigator (PI) and Laboratory Manager
(612)626-7889
amyrbo@umn.edu



10/16/2013

Shannon Lotthammer
Minnesota Pollution Control Agency
Division Manager
Environmental Assessment and Outcomes
(651)757-2537
shannon.lotthammer@state.mn.us



11/03/2013

Edward Swain, PhD
Minnesota Pollution Control Agency
Project Manager
Research Scientist 3
(651)757-2772
edward.swain@state.mn.us

Section A.1: Approvals (Continued)

Approval: Date:

10/11/2013

Patricia Engelking
Minnesota Pollution Control Agency
Contract Manager
Planner Principal State
(651)757-2340
pat.engelking@state.mn.us

11/27/2013

William Scruton
Minnesota Pollution Control Agency
QA Coordinator
(651)757-2710
bill.scruton@state.mn.us

10/14/2013

Paul Moyer
Minnesota Department of Health
Manager, Public Health Laboratory
(651)201-5669
paul.moyer@state.mn.us

Section A.1: Approvals (Continued)

Approval: Date:

11/01/2013

Daniel Engstrom
Science Museum of Minnesota
Director of the St. Croix Field Station
(651)433-5953 X11
dengstrom@smm.org

10/11/2013

John J. Pastor, Ph.D.
Professor, University of Minnesota, Duluth, Biology
Principal Investigator
(218)726-7148
jpastor@d.umn.edu

Section A.2: Table of Contents

Contents

Section A.3: Distribution List

The individuals listed below will receive copies of the approved QAPP and subsequent revisions:

Amy Myrbo, Ph.D., *University of Minnesota -Twin Cities - LacCore/LRC, (612) 626-7889*
Nathan Johnson Ph.D., *University of Minnesota - Duluth, (218) 726-6435*
John Pastor Ph.D., *University of Minnesota - Duluth, (218) 726-7001*
Shannon Lotthammer, *MPCA, (651) 757-2537*
Edward Swain, Ph.D., *MPCA, (651) 757-2772*
Patricia Engelking, *MPCA, (651) 757-2340*
William Scruton, *MPCA, (651) 757-2710*
Paul Moyer, *Minnesota Department of Health, (651) 201-5669*
Jeff Brenner, *Minnesota Department of Health, (651) 201-5353*
Shane Olund, *Minnesota Department of Health, (651) 201-5357*
Daniel Engstrom, Ph.D., *Science Museum of Minnesota, (651) 433-5953 X11*
Jill Coleman Wasik, *Science Museum of Minnesota, (651) 433-5953 X16*

Section A.4: Project Organization and Responsibility

Section A.4.1: The University of Minnesota – Twin Cities Principal Investigator

The Principal Investigator will:

- Review and approve the Quality Assurance Project Plan (QAPP) including subsequent revisions.
- With guidance from the MPCA Project Manager, design, develop, and implement the 2013 Field Survey, maintaining project notebooks and recording data in an appropriate database.
- Provide administrative direction to assigned staff as needed.
- Critically examine all data generated for the project and annotate the data with any concerns.
- Transfer all final data, including annotations, to the MPCA Project Manager.
- Make preliminary interpretations of the data.
- Prepare reports to the MPCA that summarize the experiments, results, preliminary interpretations, and include an attachment of all final data in electronic database format.
- At their discretion, publish results from the project in a peer-reviewed journal.

Section A.4.14: University of Minnesota – Duluth: Nathan Johnson Ph.D. - Civil Engineering Assistant Professor

The Assistant Professor will:

- Communicate frequently with the PI and MPCA Project Manager to facilitate research responsibilities and study goals as outlined in project work order.
- Provide direct supervision and project assignment to assigned staff.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Prepare reports.
- Review the QAPP including subsequent revisions.
- At his discretion, publish results from the project in a peer-reviewed journal.

Section A.4.3: University of Minnesota – Duluth: Dr. John Pastor Ph.D. – Department of Biology Assisting Researcher

The Principal Investigator will:

- Review and approve the Quality Assurance Project Plan (QAPP) including subsequent revisions.
- Collaborate with Dr. Nathan Johnson and assigned staff as outlined in the project work order.
- Critically examine all data generated for the project and annotate the data with any concerns.

Section A.4.4: The MPCA Division Manager

The MPCA Division Manager will:

- Provide administrative direction to assigned staff as needed.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Review and approve the QAPP including subsequent revisions.
- Conduct annual performance appraisals of assigned staff specific to their position description relating to the Sulfate and Wild Rice Project.

Section A.4.5: The MPCA Project Manager

The MPCA Project Manager will:

- Provide administrative direction to assigned staff and to the MPCA QA/QC coordinator as needed.
- Implement the elements of the Project as well as any required quality control measures.
- Review and approve the QAPP including subsequent revisions.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Oversee the preparation of all Project reports to include measurable benchmarks, problems encountered regarding QA/QC, and recommended changes in procedures.
- Review all project deliverables and strategies.
- Provide direct supervision and project assignment to assigned staff.
- Provide technical direction for the preparation of work plans and the tasks to be performed.
- Review invoices to ensure proper billing for services provided by the contractor(s).
- Interpret analytical data generated for the project.
- Represent the data using modeling procedures approved for use in the project.
- Represent the MPCA in meetings.
- Publish the results from the project in peer-reviewed journals.

Section A.4.6: The MPCA Contract Manager

The MPCA Contract Manager will:

- Implement the elements of the project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Review and approve the QAPP including subsequent revisions.
- Provide technical direction for the preparation of work plans and the tasks to be performed.
- Review invoices to ensure proper billing for services provided by the contractor(s).
- Represent the MPCA in meetings.

Section A.4.7: MPCA QA Coordinator

The MPCA QA Coordinator will:

- Represent the MPCA with the contractor(s) ensuring adequate exchange of information regarding Project responsibilities and effective functioning of the analytical Project.
- Coordinate analytical needs and projections, analytical data reports from the contractor, and resolution of problems arising from contract provisions with the analytical laboratory and MPCA staff.
- Review and approve the QAPP including subsequent revisions.
- Notify the contractor of updates and changes in analytical techniques or requirements of federal and state regulatory Projects.
- Update and distribute the Sulfate and Wild Rice QAPP when deemed necessary.
- Provide an overview to the Project Manager of analytical results and quality control data to ensure the laboratory has met Project requirements.

Section A.4.8: MDH Public Health Laboratory Manager

The MDH Public Health Laboratory Manager will:

- Provide administrative direction to assigned staff and to the MDH QA Officer as needed.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Review the QAPP including subsequent revisions.

Section A.4.9: MDH Inorganic Unit Supervisor

The MDH Inorganic Unit Supervisor will:

- Ensure that the analytical requirements of the QAPP are implemented.
- Provide direct supervision and project assignment to assigned staff.
- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Provide direction for analytical requirements.
- Perform final review of analytical data reports to ensure requirements are met.
- Review and approve the QAPP including subsequent revisions.

Section A.4.10: MDH QA Officer

The MDH QA Officer will:

- Monitor and evaluate laboratory analytical activities as they pertain to this QAPP.
- Conduct and document internal audits of laboratory procedures.
- Review laboratory SOPs.
- Schedule and document pertinent Method Detection Limit studies.
- Maintain staff training records.
- Maintain the laboratory corrective action program.
- Review the laboratory elements of the QAPP.

Section A.4.11: MDH Laboratory Staff

The MDH Laboratory Staff will:

- Ensure analytical procedures are followed.
- Document the analysis and observations.
- Identify and report analytical problems to the Unit Supervisor and QA Officer.

Section A.4.12: University of Minnesota LacCore/LRC Laboratory Manager

The Laboratory Manager will:

- Provide direct supervision and project assignment to assigned staff.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Prepare reports.
- Review and approve the QAPP including subsequent revisions.

Section A.4.13: The Science Museum of Minnesota Field Station Director

The Field Station Director will:

- Provide administrative direction to assigned staff as needed.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Review and approve the QAPP including subsequent revisions

Section A.4.14: The Science Museum of Minnesota Laboratory Manager

The Laboratory Manager will:

- Provide direct supervision and project assignment to assigned staff.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Prepare reports.
- Review the QAPP including subsequent revisions.

Section A.4.15: Gustavus Adolphus Faculty and Chemistry Laboratory Manager

The Laboratory Researcher will:

- Provide direct supervision and project assignment to assigned staff.
- Implement the elements of the Project as well as any required quality control measures.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.

- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Prepare reports.
- Review the QAPP including subsequent revisions.

Section A.5: Definition/Background

In the Minnesota Rules Chapter 7050 water quality standards and use classification rule, the MPCA assigns a series of use classifications to all waters of the State of Minnesota. Water use classifications, and their accompanying narrative and numeric criteria and non-degradation provisions, make up the state's set of water quality standards. Aquatic life and recreation, industrial uses, agriculture and wildlife, and domestic consumption are some of the beneficial uses these standards are intended to protect.

Minnesota's Class 4 Agriculture and Wildlife use classification covers agricultural uses (crop irrigation and livestock uses) as well as wildlife uses. Under the Class 4A use classification, Minnesota currently has a water quality standard of ***"10 mg/L sulfate - applicable to water used for the production of wild rice during periods when the rice may be susceptible to damage by high sulfate levels."*** (Minn. R. 7050.0224, subpart 2).

This 10 mg/L sulfate wild rice standard (reported as SO_4) was adopted into the MPCA water quality standards rule in 1973. Based on testimony presented at public hearings leading to the adoption of this sulfate standard, it was intended to apply both to waters with natural wild rice stands and to waters used for paddy wild rice production. The standard was based on field observations and water chemistry correlations made by John Moyle primarily in the late 1930s and early 1940s. Dr. Moyle was a highly respected biologist with the then Minnesota Department of Conservation, and later the Minnesota Department of Natural Resources, who concluded that "No large stands of rice occur in water having sulfate content greater than 10 ppm (parts per million), and rice generally is absent from water with more than 50 ppm." The wild rice rule was based on sound scientific evidence and, to date, the MPCA has not been presented with evidence that would support amending the rule.

The next set of wild rice-related rule amendments occurred around 1997. It was during that time that the MPCA initiated rulemaking proceedings that led to the adoption of new rules governing water quality standards, standards implementation, and non-degradation standards for Great Lakes Initiative (GLI) pollutants in the Lake Superior Basin. This rule was codified as Minn. R. ch. 7052 and is now informally referred to as the "Lake Superior Basin" or the "GLI" rule. The 1997 rulemaking also included two major changes to Minn. R. ch. 7050: 1) A portion of the Lake Superior shoreline waters in the vicinity of the Grand Portage Indian Reservation was designated as Outstanding Resource Value Waters—Prohibited, in accordance with the provisions of Minn. R. 7050.0180. 2) and 22 lakes and two river segments located in the Lake Superior watershed were listed as wild rice waters (Minn. R. 7050.0470, subp. 1) and narrative language was included pertaining to wild rice under the Class 4 Agriculture and Wildlife use class (Minn. R. 7050.0224, subp. 1).

The 1997 rulemaking record reveals that originally there were 124 lake or river segments identified as wild rice waters within the 1854 Ceded Territory that were suggested for listing in Minn. R. ch. 7050 as wild rice waters. These waters were considered to be some of the more important existing and/or potential wild rice waters identified by the Fond du Lac, Bois Forte, and Grand Portage Bands. Since the provisions of the new GLI rule were specific to the Lake Superior Basin, in 1997 MPCA staff chose to limit assignment of the wild rice designation to those waters identified and agreed upon that were within the Lake Superior Basin (Minn. R.

7050.0470, subp. 1). The listing of a select number of waters as wild rice waters was intended to be part of a broader process to provide greater protection for, and greater public awareness of, the ecological importance of wild rice. These listings were also viewed as an affirmation of the MPCA's commitment to work cooperatively with Tribal governments and others concerned about wild rice waters. Inclusion of the wild rice narrative language and the rule listings were considered "first steps" toward a future statewide identification and listing of wild rice waters and the development of wild rice-related best management practices.

The 1997 rulemaking post-hearing comments noted that the 10 mg/L wild rice sulfate standard was not proposed for revision during the 1997 proceedings. In addition, the 10 mg/L sulfate standard was never intended to apply only to the 24 wild rice waters that were specifically listed in Minn. R. Ch. 7050.0470. Rather this numeric standard was intended to continue to have statewide applicability to those waters used for production of wild rice.

The MPCA is currently striving to clarify current and future implementation of the wild rice sulfate standard, which recently has come under increased questioning and contention. Based on a review of available studies and information, MPCA believes that additional wild rice plant toxicity studies are needed to evaluate the effects of sulfate and other variables on wild rice, across the full life cycle of the plant, before a revision to the numeric standard can be considered.

The research, data, and reports developed from this 2013 survey will be used by the MPCA in its decision as to whether or not a change to the existing sulfate standard is necessary, and if so, how it should be amended. In addition, the findings of this survey will also serve to enhance the overall scientific understanding of the complex ecology of natural wild rice in Minnesota, which may in turn help to guide how to more effectively protect and manage this natural asset in the future.

Section A.6: Project Descriptions

Section A.6.1: Objective

The goal of this project is to collect and analyze various types of environmental samples, as well as to document observations of the environment from selected lake, stream, and wild rice paddy field sites across a spectrum of sulfate concentrations and wild rice abundance. In particular, the selected sites for the 2013 field survey are focused on those sites where wild rice has been noted as to naturally grow now or in the past but in the presence of higher sulfate concentrations. The process by which sites were selected is beyond the scope of this QAPP. The quality objectives will generally follow the guidance outlined on the MPCA's Quality System webpage: (http://www.pca.state.mn.us/index.php/about-mpca/mpca-overview/agency-strategy/mpca-quality-system.html?expandable=1&menuid=&redirect=1). The Quality System for MPCA's environmental data describes the agency's general policy for data quality assurance. This QAPP falls under all requirements of the MPCA's quality management plan (QMP) which is approved by U.S. EPA Region 5.

Section A.6.2: Scope

The objective of the QAPP is to define the Quality Assurance and Quality Control (QA/QC) elements, procedures and responsibilities to be followed by project researchers and administrative participants of the Wild Rice Sulfate Standard 2013 Field Survey as defined in section A.4. These QA/QC elements, procedures and responsibilities are to guide the collection, transport, analysis, and data management of samples and sample results to assure sufficient precision and accuracy of results in order for them to be used for their intended purpose. The field sampling collection, preparation, and transportation procedures are described below in the body of the QAPP as well as provided in Appendix I (Dr. Myrbo's Field Sampling SOP) and Appendix E (Dr. Johnson's Peeper Sampling SOP). Analytical methods used are identified in tables 1, 2, and 3 by the chemistry performed, specific laboratory performing the analysis and the location they can be found in the Appendix of this QAPP. Analytical QA/QC elements and acceptance criteria are described below in section B. Section C documents the assessment and oversight of QA/CQ elements, and section D outlines activities for the reduction, verification, and validation of data generated throughout the field survey.

Section A.6.3: Analytical Samples

The samples are brought under chain of custody procedures to the MDH Environmental Laboratory, the University of Minnesota LacCore/LRC Laboratory, the Science Museum of Minnesota St. Croix Watershed Research Station Laboratory (SCWRS), or UMD Department of Civil Engineering. The samples are labeled to allow for identification of each sample specific to the site where the sample was taken and by the type of analyses being requested. This information allows the laboratory to use the proper method when analyzing these samples and to produce identifiable record of results. Specific instructions on sampling procedures including collection, preservation and transportation, are provided in Section B.1. The lists of target analytes are provided below in Tables 1, 2, and 3. Table 4 lists all non-analytical sample analyses or sample collections.

Table 1: Proposed Target Analytes in Surface Water

Target Analyte	Method Reference	Report Limit	Responsible Laboratory	Method Location
Alkalinity as CaCO3	SM2320B	10.0 mg/L	MDH Inorganic	Appendix C
Ammonia-Nitrogen	EPA 350.1	0.050 mg/L	MDH Inorganic	Appendix C
Chloride	EPA 300.1	0.050 mg/L	MDH Inorganic	Appendix C
Conductivity	EPA 120.1	0.200 micromhos/cm	MDH Inorganic	Appendix C
Nitrate + Nitrite Nitrogen	EPA 353.2	0.050 mg/L	MDH Inorganic	Appendix C
Sulfate	EPA 300.1	0.050 mg/L	MDH Inorganic	Appendix C
Total Nitrogen	SM4500N B	0.050 mg/L	MDH Inorganic	Appendix C
Total Phosphorus	SM4500P I	0.010 mg/L	MDH Inorganic	Appendix C
Dissolved Calcium	EPA 200.7	2.00 mg/L	MDH Inorganic	Appendix C
Dissolved Iron	EPA 200.8	0.005 mg/L	MDH Inorganic	Appendix C
Dissolved Magnesium	EPA 200.7	2.00 mg/L	MDH Inorganic	Appendix C
Dissolved Potassium	EPA 200.7	0.500 mg/L	MDH Inorganic	Appendix C
Dissolved Sodium	EPA 200.7	0.500 mg/L	MDH Inorganic	Appendix C

Table 2: Target Chemical Analytes in Sediment

Target Analyte	Method Reference	Report Limit	Responsible Laboratory	Method Location
Acid Volatile Sulfides	SM4500-S2J	0.657 mg/kg dry	MDH Inorganic	Appendix C
Loss-on-Ignition (Water Content, Organic Matter, Carbonate Content, Inorganic Matter)	N/A	0.1 mg/kg	LacCore/LRC	Appendix H
% Dry Weight	SM4500-S2J	0.0001 g	MDH	Appendix C
Total Carbon	N/A	TBD	LacCore/LRC	Appendix H

Total Nitrogen	N/A	TBD	LacCore/LRC	Appendix H
Total Sulfur	N/A	TBD	LacCore/LRC	Appendix H
Total Inorganic Carbon	N/A	TBD	LacCore/LRC	Appendix H
Total Phosphorus	QuikChem method 10-115-01-1A	0.0125 mg/L	SCWRS	Appendix F
Phosphorus Fractionation	QuikChem method 10-115-01-1A	0.0125 mg/L	SCWRS	Appendix F
Extractable Metals for ICP-MS (Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Ti, V, Zn)	EPA 6020A	TBD	SCWRS and Gustavus	Appendix F and G

Table 3: Proposed Target Analytes in Sediment Porewater – MDH Environmental Inorganic Laboratory and UMD Civil Engineering

Target Analyte	Method Reference	Report Limit	Responsible Laboratory	Method Location
Ammonia-Nitrogen	EPA 350.1	0.050 mg/L	MDH Inorganic	Appendix C
Chloride	EPA 300.1	0.050 mg/L	MDH Inorganic	Appendix C
Dissolved Organic Carbon	SM5310C	1.00 mg/L	MDH Inorganic	Appendix C
Nitrate + Nitrite Nitrogen	EPA 353.2	0.050 mg/L	MDH Inorganic	Appendix C
Sulfate	EPA 300.1	1.00 mg/L	MDH Inorganic	Appendix C
Sulfate	EPA 300.1	1.00 mg/L	UMD Civil Engineering	Appendix D
Sulfide	SM4500-S2E	0.010 mg/L	MDH Inorganic	Appendix C
Sulfide	SM4500-S2D	0.010 mg/L	UMD Civil Engineering	Appendix D
Total Nitrogen	SM4500N B	0.050 mg/L	MDH Inorganic	Appendix C
Total Phosphorus	SM4500P I	0.010 mg/L	MDH Inorganic	Appendix C
Calcium	EPA 200.7	2.00 mg/L	MDH Inorganic	Appendix C
Iron	EPA 200.8	0.005 mg/L	MDH Inorganic	Appendix C
Iron	EPA Method 200.8 Using the ELAN 6000 ICP-MS	0.005 mg/L	UMD Civil Engineering	Appendix D
Magnesium	EPA 200.7	2.00 mg/L	MDH Inorganic	Appendix C
Potassium	EPA 200.7	0.500 mg/L	MDH Inorganic	Appendix C
Sodium	EPA 200.7	0.500 mg/L	MDH Inorganic	Appendix C
Arsenic	EPA 200.8	0.001 mg/L	MDH Inorganic	Appendix C
Boron	EPA 200.7	0.020 mg/L	MDH Inorganic	Appendix C
Cobalt	EPA 200.8	0.001 mg/L	MDH Inorganic	Appendix C
Copper	EPA 200.8	0.010 mg/L	MDH Inorganic	Appendix C
Copper	EPA Method 200.8 Using the ELAN 6000 ICP-MS	0.010 mg/L	UMD Civil Engineering	Appendix D

Manganese	EPA 200.8	0.010 mg/L	MDH Inorganic	Appendix C
Molybdenum	EPA 200.8	0.001 mg/L	MDH Inorganic	Appendix C
Selenium	EPA 200.8	0.001 mg/L	MDH Inorganic	Appendix C
Zinc	EPA 200.8	0.010 mg/L	MDH Inorganic	Appendix C
Zinc	EPA Method 200.8 Using the ELAN 6000 ICP-MS	0.010 mg/L	UMD Civil Engineering	Appendix D
Silica	SM4500 SiO_2 C	0.500 mg/L	MDH Inorganic	Appendix C

Table 4: Non-Analytical Sample Analysis and Characterizations

Target Environmental Measurement	Responsible Laboratory	Method Location
Wild Rice Phytolith Analysis in Sediment	LacCore/LRC	Appendix H
Organic Grain Size in Sediment	LacCore/LRC	Appendix H
On site surface water Sonde Readings (conductivity, temperature, pH, DO)	LacCore/LRC	Appendix H
Surface Water Transparency	LacCore/LRC	Appendix H
Sediment Temperature Profile	LacCore/LRC	Appendix H
Mature Wild Rice Plant Pressings	LacCore/LRC	Appendix H
Aquatic Vegetation Identification at field site	LacCore/LRC	Appendix H

Section A.6.4: Intended Data Usage

The data will be used to aid the MPCA in deciding whether or not to recommend a change to the existing sulfate standard and how the standard should be revised if a change is recommended.

Section A.6.5: Technical Reports

Within one week of each site visit, the PI will provide MPCA study staff with: a list of sites visited including dates, GPS coordinates, access issues and other site visit notes. The PI is responsible for producing analytical results in database format to be delivered to the MPCA by Oct 16th, 2013 or as the contracted laboratories make the data available. The PI will produce a final report that documents field and laboratory methods, any changes in methods over time, cross-calibration of data between 2011 and 2012 field seasons, sites sampled, data collected, database developed, populated content of the database, summary data statistics, quality assurance data, outlier data as the result of human error, and maps showing the distribution of sites from all of the MPCA-sponsored wild rice field surveys (2011 preliminary survey, 2012 reconnaissance, 2012 field survey, and 2013 field survey) by December 19th, 2013 as indicated in the 2013 Wild Rice Sulfate Standard Field Survey Category 4 Project Work Plan. Two to three draft reports will be submitted to MPCA staff for commenting at agreed upon times before a final report is produced. The PI will also present results at one or more meetings as requested by the MPCA project manager.

Along with the integration of data and additional considerations produced from other areas of the Wild Rice Sulfate Standard Study, MPCA project staff will use the data produced by the 2013 Field Survey to assess the appropriateness of the current 10mg/L sulfate standard in protecting wild rice, in order make a recommendation as to if and how it should be amended. A technical support document will be developed to support this decision.

Section A.7: Quality Assurance Objectives and Criteria

Section A.7.1: Overview

Quality assurance objectives are developed for field sampling, chain of custody, laboratory analysis and reporting (see detailed procedures in Section B.2 and B.3). Meeting these objectives will provide the MPCA with defensible data and results.

The sample collection technicians will be responsible for field sampling and chain of custody until the laboratory accepts samples. Specific procedures to be used for sampling, quality control, audits, preventive maintenance and corrective actions are described in other sections of this document. The purpose of this section is to define quality assurance goals for precision, accuracy and completeness. Establishing these goals allows the State to judge the adequacy of the results and whether corrective actions are necessary.

The quality assurance objectives to be met for both field operations and laboratory activities are discussed below.

Laboratory reports include the date of sampling, the date of analysis, the signed Chain of Custody form, a narrative of the analysis which notes items that are outside the laboratory QC limits, and the analytical results for the collected sample. In addition to the analytical results, the reports include the percent recoveries (% R) of laboratory control sample/laboratory control sample duplicates, matrix spikes, and standard reference material and the relative per cent differences (RPD) between duplicates.

Laboratory QC elements and acceptance criteria are detailed in Tables 5, 6, 7 and 8.

Section A.7.2: Blanks

The samplers will use field blanks (sample bottles and laboratory DI water) while sampling. Field blanks are submitted at a 5% rate to the laboratory. Field blanks results verify that the field sampling and laboratory procedures are free of contamination and do not contaminate blank samples.

The laboratory uses method blanks to verify the extraction procedures, glassware, and instrument conditions have background below the laboratory reporting limits. The method blanks are reported with MPCA samples to allow the project manager to determine that laboratory contamination or analytical error could cause a false positive. The laboratory performs method blanks at a rate of one for each analytical batch of twenty samples (5%) or less to ensure a contaminant-free environment.

Section A.7.3: Duplicate Samples

As is the case for field blanks, duplicate samples are collected as necessary to protect the integrity of the sampling investigation. Duplicates are collected by co-locating samples. Duplicate sample analyses provide a check on sampling and analytical reproducibility, or precision. The laboratory also prepares and analyzes replicate samples to gain a measure of reproducibility. MPCA has a relative percent difference (RPD) goal for duplicates of 25% in waters and 50% in sediments

Section A.7.4: Matrix Spike Samples

Spiked samples will not be collected in the field but MPCA does submit adequate samples to ensure the laboratory has enough sample to allow for a spike analysis. The laboratory uses Matrix Spike (MS) recoveries to measure accuracy in the analyses. Laboratory-generated limits for spike recoveries are used in validation of data (when required). MPCA policy requires a 10% rate of spikes for environmental samples.

Section A.7.5: Laboratory Activities

The quality assurance objectives for accuracy, precision, completeness, representativeness, reporting limits, and comparability to be met by the laboratory are described in the laboratory's Quality Assurance Manual (QAM), if available.

Section A.7.6: Definitions of Precision, Accuracy, Representativeness, Comparability, and Completeness

Where possible, laboratory precision is measured through the collection and analysis of duplicate samples. The result for the duplicate sample is compared to the result of the known sample. The relative percent difference (RPD) between the known sample result and the duplicate sample result is calculated according to the following formula:

$$RPD = \frac{(Sample\ Conc. - Duplicate\ Conc.)*200}{(Sample\ Conc. + Duplicate\ Conc.)}$$

Precision can also be determined between the results of a laboratory control sample (LCS)/laboratory control sample duplicate (LCSD) pair. RPD results should be <25% for water samples and <50% for sediment samples for the data to be acceptable.

Section A.7.6.1: Accuracy

The accuracy of the measurement is gauged through the analyses of surrogate spikes, matrix spike (MS), and/or laboratory control sample (LCS)/laboratory control sample duplicate (LCSD). Surrogate compounds are spike into every sample prior to extraction and analysis. Where possible, a MS sample is collected. If a MS cannot be analyzed, an LCS/LCSD pair may be used to

measure accuracy. The percent recovery is determined by comparing the spiked sample concentration to the environmental (un-spiked) sample concentration. The formula for determining percent recovery is as follows:

$$\%R = \frac{(\text{Spiked Sample Conc.} - \text{Environmental Sample Conc.}) * 100}{\text{Spiked Concentration Added}}$$

Section A.7.6.2: Representativeness

Representativeness of the data set is the measure that expresses the degree to which the data accurately represents the population as a whole. The methods for sample collection in the field, sample preservation, transportation to the laboratory, sample preparation, and sample analysis are reviewed to determine if appropriate procedures were followed. If the procedures as described in this QAPP were followed, sample results are considered representative of the site.

Section A.7.6.3: Comparability

Comparability is the degree of confidence that one data set can be compared to another data set and whether the data sets can be combined and used for decision-making purposes. The level of comparability between data sets is determined by reviewing sample collection and handling procedures, sample preparation and analytical procedures, holding times, and quality assurance protocols. When a large difference in one of the methods or procedures exists, the comparability of the data is considered low. If all of the procedures were followed, data from the same site is considered comparable.

Section A.7.6.4: Completeness

Completeness is measured by determining the ratio of valid sample results compared to the total number of samples for a specific matrix. During data verification, the data completeness is determined by the following equation:

$$\%\text{Completeness} = \frac{\text{Number of Valid Results} * 100}{\text{Number of Samples Tested}}$$

A completeness of 90% in a year must be obtained in order for a laboratory report to be considered acceptable. If the data set does not meet at least 90% completeness, the data are rejected. If the laboratory is at fault and they will be responsible for securing the re-collection and re-analysis of samples.

Section A.8: Specialized Training/Certifications

Section A.8.1: Field

Personnel assigned to the Wild Rice Project will meet the educational, work experience, responsibility and training requirements for their positions. At a minimum, field personnel will have been instructed in field safety training, the monitor manufacture's operational manuals, field standard operating procedures (SOPs), a Defensive Driving course, and the Project QAPP. Records on personnel qualifications and training will be maintained in personnel files and will be accessible for review during audit activities.

Section A.8.2: Laboratory

Laboratory personnel have been trained in proper analytical techniques. They also receive annual refresher training on such items as laboratory safety, right to know, and emergency procedures. The documentation of this training is maintained in the Laboratory Manager's office or in the laboratory's QA Office.

Section A.9: Record Keeping

The State of Minnesota has a structured record management retrieval system that allows for the efficient archive and retrieval of records. All information considered as documentation and records will be retained for 10 years from the date of generation. However, if any litigation, claim, negotiation, audit or other action involving the records has been started before the expiration of the 10-year period, the records must be retained until completion of the action and resolution of all issues which arise from it, or until the end of the regular 10-year period, whichever is later. The laboratory SOP for records retention indicates that all data documentation, records, protocols, and final reports are stored either on-site at the laboratory or off-site in secure storage. The records are retained for a period of not less than 10 years.

Section B: Data Generation and Acquisition

Section B.1: Sampling Design

In consultation with the MPCA project manager, sites for the 2013 field survey were selected based on considerations of previous field survey work conducted in 2011 and 2012, a preliminary field survey and the field and lab data collected as part of the reconnaissance project conducted May-June 2012. The process by which sites were selected for the 2013 field survey is beyond the scope of this QAPP

Section B.2: Sampling Procedures

Prior to sample collection, field personnel coordinate with the laboratory to assure that appropriate equipment and supplies are available to meet the sampling need. After collection, the samples will be shipped or delivered to the laboratory for analysis.

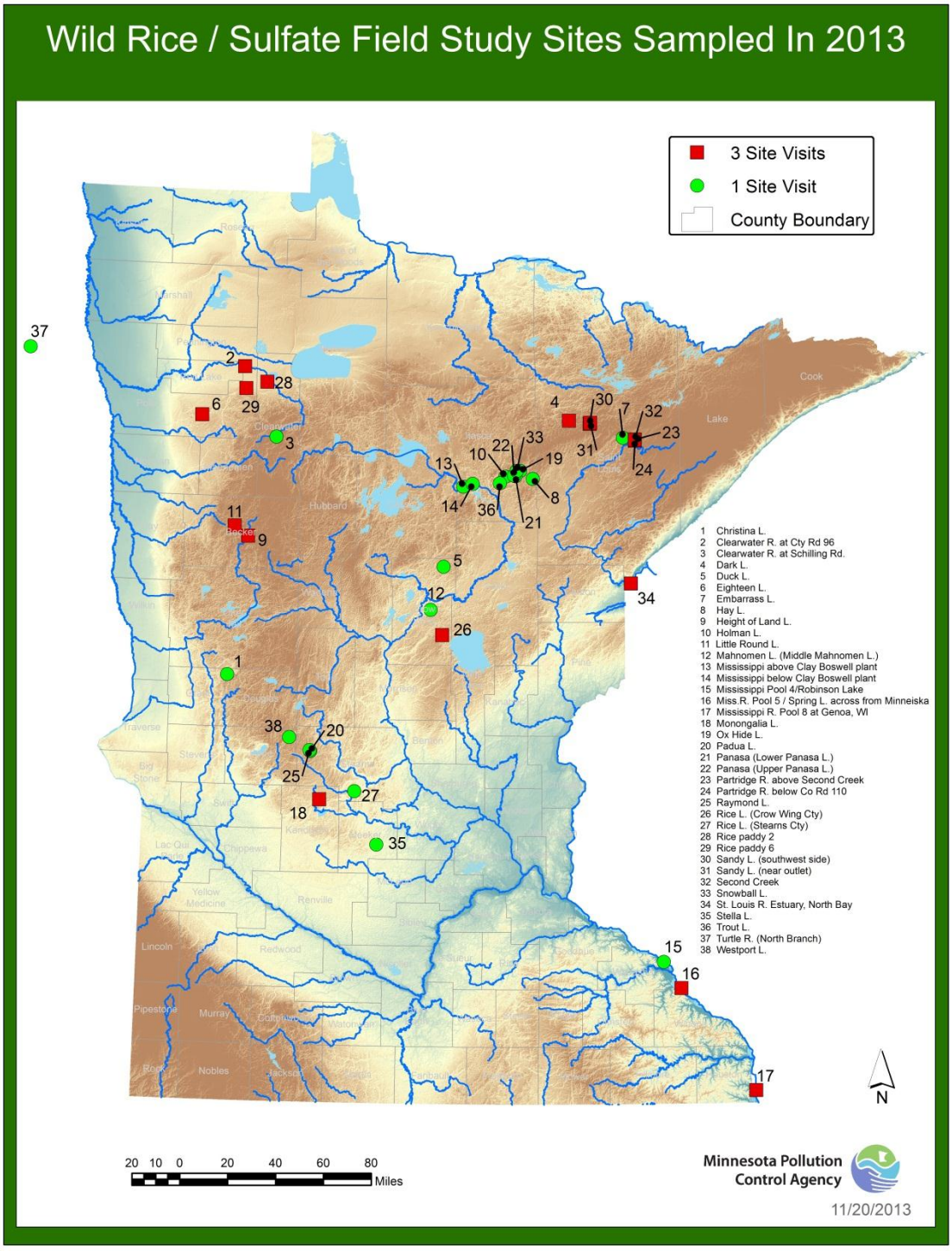
As part of the overall project, approximately 35 to 40 sites will be visited. Just under half of these sites will be visited and sampled intensively (three times during the summer/ early fall of 2013). An additional 21 sites will be sampled once in late summer/early fall of 2013. Samples of surface water, sediment, mature wild rice plants (if available), sediment porewater, and temperature profile will be collected and analyzed to determine various characteristics. Figure 1 below lists the names, general locations and numbers of times each of the sites are to be sampled by Dr. Myrbo and her field crew during the summer/fall of 2013

Teams of two technicians will make approximately 75 total visits during the 2013 survey to sites across Minnesota to collect data and samples from selected surface water bodies (see Figure 1), including lakes, rivers, and commercial wild rice paddies. Crews will locate access to sites using information and contacts developed during the 2011 Preliminary Field Survey and 2012 reconnaissance, displayed on base maps on project iPads. Using a canoe or motorboat, crews will sample water, sediment, mature wild rice plants, and sediment porewater within a wild rice bed or, in the absence of wild rice, in a location that could support wild rice based on the presence of aquatic plants that have similar habitat requirements to wild rice. Crews will follow the sampling procedures established in the QA/QC documentation. Crews will record the GPS position at each sampling site, and measure conductivity, temperature, pH, and dissolved oxygen using a sonde; collect a surface water sample; collect six sediment cores of ~50 cm length; and survey and identify aquatic vegetation. On shore, water samples will be filtered (except for TP/TN) and split for various water chemistry analyses to be conducted by the MDH Environmental Laboratory. The pH of the surface sediment will be measured. Two of the sediment cores will be used to produce two porewater samples using Rhizon-brand samplers connected to an evacuated, anaerobic serum vial, one of which will be pre-loaded with zinc acetate (vials supplied by MDH). Three sediment cores will be extruded from the top to a depth of 10 cm, and the extruded portions immediately combined under a nitrogen atmosphere and homogenized together, and subsampled for acid-volatile sulfide (AVS) sample analysis and immediately frozen using dry ice,

and the remainder of the sample placed on water-ice for other sediment analyses as described below ("sample analysis"). One sediment core will be archived for possible future analysis. If found at the site, two mature wild rice plants will be pressed according to guidance from the University of Minnesota Herbarium. Crews will log samples and assign ID numbers, and fill out an MDL and UMN chain of custody paperwork. As appropriate and as indicated in the QA/QC documentation or as requested by the MPCA project manager, crews will return samples to University of Minnesota laboratory and transfer samples to MDHL or other lab within established holding time requirements. Field survey expenses shall conform to the 2013 Wild rice sulfate standard field survey Category 4 Master Work Contract. The field sampling methods to be implemented by Dr. Myrbo and her field crew described above are documented in the "Field Protocol for MPCA-SO4 Field Sampling by LacCore/LRC" located in Appendix I

Additional sediment porewater sampling will be conducted by Dr. Nathan Johnson of the University of Minnesota Duluth's Civil Engineering Department. This porewater sampling will use a sampling instrument called a "peeper" that allows for the development of a stratigraphic profile of various analytes in porewater located around the rooting zone of wild rice plants. This will compliment Dr. Myrbo's porewater sampling using the Rhizon-brand sampler that provides an integrated porewater sample rather than one stratified by depth. Peepers will be deployed once a month at two of the sites that are sampled by Dr. Myrbo's field crew throughout the wild rice growing season, from May through September. The sampling method is provided in Appendix E, with the duties and responsibilities of Dr. Johnson are detailed in the Wild Rice Categories 1 & 2 study: UMD Project Work Plan.

Figure 1: Potential 2013 Field Sampling Locations – Intensive (Red) and Single Visit (Green) Sites



Section B.3: Sample Custody

Section B.3.1: Overview

Sample possession must be traceable from the time samples are collected until they are disposed of. To maintain and document sample possession, chain of custody (COC) procedures are followed.

Section B.3.2: Field Custody Procedures

Trained field personnel collect the samples (see Section B.1). The field personnel either have the samples in their possession, in their view, in a secured area that only they have access to, or turn custody over to another individual who has signed the chain of custody (COC) form (See Attachment 3 for an example COC form). The COC is the record of all individuals who come in contact with the samples. A COC has the following information present:

A. Date and time of sampling,
B. Name of sampler,
C. Identification number of the samples,
D. Analytical methods requested,
E. Project name,
F. Signature of the sampler, and
G. MPCA contact name and phone number.

Sample custody is maintained from collection through analysis. The samples are cooled on ice, or are frozen with dry ice, in a cooler. The chain of custody form is signed by the sampler and double zip-locked and taped to the inside lid of the cooler. The sampler and the laboratory keep a copy of the bill of lading as proof of custody in shipment. Records of custody are maintained by the MPCA within the site files.

Section B.3.3: Laboratory Custody

Laboratory custody procedures are usually described in the laboratory QAM, if available. The laboratory signs the COC when the samples are received. The laboratory verifies the COC is correctly filled out and all samples are accounted for (and not broken). Any problems that occur upon receipt of the samples will cause the sample clerk at the laboratory to immediately contact the MPCA Project Manager or QA Coordinator. The MPCA will decide if the samples are to be run depending on the problem. The laboratory logs in the samples into the laboratory LIMS system. The system assigns a unique number to each sample. The log-in numbers are then used to track the sample at the laboratory.

The laboratory stores the samples in a secure refrigerated area that maintains the samples at 4° +/- 2° C. Frozen samples remain frozen until sample analysis is performed. The sample holding area is secure from unauthorized personal having access to the samples. The samples are removed by an analyst for extraction/digestion, the extraction/digestion performed, and any remaining sample placed back in the refrigerator. The laboratory disposes of the samples, except in case of very hazardous samples, which are then returned to the site or lab-packed for disposal at an appropriate facility.

Section B.4: Analytical Methods

Information on the analytical methods to be used in this study is detailed in Tables 1, 2, and 3. Their corresponding analytical methods are identified by laboratory and their location in the Appendices of this QAPP. Corrective actions taken in the process of field sampling and analyzing samples are documented by the laboratory managers or staff and are ultimately reported to Dr. Myrbo and the appropriate MPCA Project management staff for the final decision.

Section B.5: Quality Control

Field and laboratory QC checks are identified in Table 5. The frequency of analysis and the control limits are also listed. If the results don't meet the QC acceptance criteria, corrective actions are defined.

Section B.5.1: QC Types

Table 5: Quality Control Elements

QC Type	Surface Water	Sediment	Sediment Porewater
Blanks			
Field Blanks	1 per batch	1 per batch	1 per batch
Method Blanks	1 per batch	1 per batch	1 per batch
Spikes			
Laboratory Control Sample	1 per batch	1 per batch	1 per batch
Matrix Spike	1 per batch	1 per batch	1 per batch
Calibration Checks	1 per batch	1 per batch	1 per batch
Duplicates			
Matrix Spike Duplicates	1 per batch	1 per batch	1 per batch
Laboratory Control Sample Duplicates	1 per batch	1 per batch	1 per batch

Table 6: QC Acceptance Criteria for Target Analytes in Surface Water

Target Analyte	Blanks	LCS (%R)	MS (%R)	Duplicates (RPD)	Laboratory	Appendices
Alkalinity as CaCO3	<RL	90 – 110	85 – 115	25	MDH	Appendix C
Ammonia-Nitrogen	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Chloride	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Nitrate + Nitrite Nitrogen	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Sulfate	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Total Nitrogen	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Total Phosphorus	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Dissolved Calcium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Iron	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Magnesium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Potassium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Sodium	<RL	85 – 115	85 – 115	25	MDH	Appendix C

Table 7: QC Acceptance Criteria for Target Analytes in Sediment

Target Analyte	Blanks	LCS (%R)	MS (%R)	Duplicates (RPD)	Laboratory	Appendix
Acid Volatile Sulfides	<RL	70-130	80-120	50	MDH	Appendix C
Loss-on-Ignition (Water Content, Organic Matter, Carbonate Content, Inorganic Matter)	<RL	70-130	80-120	50	LacCore/LRC	Appendix H
Total Carbon	<RL	70-130	80-120	50	LacCore/LRC	Appendix H
Total Nitrogen	<RL	70-130	80-120	50	LacCore/LRC	Appendix H
Total Sulfur	<RL	70-130	80-120	50	LacCore/LRC	Appendix H
Total Inorganic Carbon	<RL	70-130	80-120	50	LacCore/LRC	Appendix H
Total Phosphorus	<RL	70-130	80-120	50	SCWRS	Appendix F
Phosphorus Fractionation	<RL	70-130	80-120	50	SCWRS	Appendix F
Extractable Metals for ICP-MS (Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ag, Na, Ti, V, Zn)	<RL	70-130	80-120	50	SCWRS/Gustavus	Appendix F and G

Table 8: QC Acceptance Criteria for Target Analytes in Porewater

Dissolved Organic Carbon	Blanks	LCS (%R)	MS (%R)	Duplicates (RPD)	Laboratory	Appendix
Sulfide	<RL	90 – 110	85 – 115	25	MDH	Appendix C
Sulfate	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Potassium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Magnesium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Dissolved Calcium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Chloride	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Boron	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Total Phosphorus	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Dissolved Sodium	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Total Nitrogen	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Ammonia-Nitrogen	<RL	90 – 110	90 – 110	25	MDH	Appendix C
Nitrate + Nitrite	<RL	85 – 115	85 – 115	25	MDH	Appendix C
Metals Fe, Cu, Zn, Co, Ni, Mn, Mo, Se, As	<RL	85 – 115	85 – 115	25	MDH	Appendix C

Section B.5.1.1: Field Blanks

Field blanks are collected to show any bias that is related to collection equipment or transport of samples from the field to the laboratory. Field blanks are collected throughout the season at 5% of the total sites visited. If there is contamination in the field blank but not in the samples, no action is required. Any positive result in an environmental sample which is associated with a positive result detected in a field blank is evaluated. If the environmental sample result is less than X5 the concentration detected in the field blank, the report level is raised to the concentration found in the sample. If the environmental sample result is greater than X5 the concentration found in the field blank, no qualification is necessary. However, an explanation of the rational should be provided in the narrative accompanying the report.

Section B.5.1.2: Method Blanks

One method blank is prepared and analyzed with each batch of up to 20 samples to demonstrate that there are no interferences from the glassware, reagents, and analytical system. Target analytes of concern should not be present in the method blank at the report level concentration. If any method blank shows target analytes above the report level, an instrument blank should be analyzed to demonstrate that there was no carry-over from standards or samples. If there was carry-over, clean the analytical system and re-inject the method blank. If the method blank contamination cannot be attributed to carry-over, the samples that were associated with the blank should be re-prepared and re-analyzed.

Section B.5.1.3: Matrix Spikes (MSs)

Matrix spikes are used to determine if there are any effects related to the sample matrix. One spike should be spiked, prepared, and analyzed per batch of up to 20 samples. The % recoveries of the MS are used to measure accuracy of the analysis. The % recoveries should be within the ranges listed in Tables 6, 7, and 8.

Section B.5.1.4: Laboratory Control Sample (LCS)

A laboratory control sample (LCS) is an aliquot of clean matrix, the same matrix as the environmental samples. One LCS is prepared with each batch of up to 20 samples. The LCS is spiked with the same target analytes and at the same concentration as the MS. The % recoveries of the LCS are used to show that the analysis is in control if there is a matrix effect associated with the analysis of the sample matrix in the MS. The % recoveries should be within the ranges listed in Tables 6, 7, and 8.

Section B.5.1.5: Field or Laboratory Duplicates

Field and laboratory duplicates are used to measure precision. One pair should be extracted and analyzed per ten samples or less. The RPD should be less than or equal to the values listed in Tables 6, 7, or 8.

Section B.5.1.6: Out-of-Control Situations

When the out-of-control situations listed in Sections B.5.1.3 through B.5.1.5 occur, the failing analysis should be repeated. If the re-analysis meets QC criteria, report the second analysis. If the re-analysis still does not meet criteria, the affected samples should be re-prepared and re-analyzed. If the results of the re-analysis of the MS still fail to meet criteria and the result of the LCS is acceptable, then the problem is related to matrix and the QC batch requirements are considered to have been met. Report the results of the batch and qualify the result of the environmental sample chosen for QC purposes as estimated. If the results for the LCS fail again, instrument maintenance is required. After the maintenance has been completed, another initial calibration must be performed.

Section B.6: Instrument/Equipment Testing, Inspection, and Maintenance

Section B.6.1: Field Equipment

Delays in project schedules, poor output in performance, and erroneous results in investigative operations can result from improperly maintained equipment. Therefore, preventative maintenance of field equipment is performed routinely before each sampling event. More extensive maintenance is performed based on hours of use and manufacturer recommendations. Spare parts for all field equipment as well as back up instruments are kept at the University of Minnesota or in the field vehicle. The field staff perform preventative maintenance on a routine schedule on all field equipment for the MPCA. Standardized field sampling equipment will be maintained by the field staff.

Section B.6.2: Laboratory Equipment

The protocols for testing, inspection, and maintenance of laboratory equipment are addressed in the laboratory QAMs, if available. Additionally, the laboratory's standard operating procedures (SOPs) present the specific protocols to be followed as part of the analysis for the program. Preventative maintenance steps employed by the laboratory are described in the laboratory QAM, if available. In general, the preventative maintenance is performed on a scheduled basis on all instruments in the laboratory. The preventive maintenance performed is documented in the instrument maintenance logbooks kept at the instrument. Irregularities noted during operations are traced through the maintenance logbook to allow for efficient corrective action to solve problems. Analysts are trained in preventive maintenance of their assigned instruments. The laboratory utilizes in-house service technicians in the event of instrument failures. Contracts are maintained on the computer hardware and software. Backup instrumentation is generally available if a specific analytical system becomes unavailable.

Section B.7: Instrument/Equipment Calibration and Frequency

Section B.7.1: Overview

This section discusses calibration procedures for field and laboratory instruments to be used for the Project. All laboratory equipment used for analytical determinations is subject to periodic inspection and calibration. Frequency of calibration is based on the type of equipment, inherent stability, manufacturer recommendations, and intended use.

Section B.7.2: Field Procedures

The field equipment used by the Project staff is calibrated according to procedures described in the manufacturing instructions and/or Project SOPs.

Section B.7.3 Laboratory Procedures

The calibration procedures followed by the laboratory are outlined in the Laboratory QAMs (if available) and SOPs. The basic procedure for the analyses is to calibrate the analytical instruments at five levels. One of the levels must be at or below the report level for the individual target analyte. The initial curve must have a coefficient of ≥0.99 or a %RSD of ≤20%. The five-point initial calibration curves are verified with an external source calibration standard and then routinely (as specified in the MDH Certification Rule or laboratory SOP) with a calibration verification check standard. All calibration standards must have a percent difference (%D) of <15%.

Section B.8: Inspection/Acceptance of Supplies and Consumables

A Project staff person inspects all supplies and consumables for integrity and suitability for use. Any supply or consumable judged to be of inferior quality or not suitable for the intended use is rejected. Sample containers are pre-certified as clean by the laboratory.

All chemicals and solvents used in the laboratory are inspected to verify that they are of the appropriate grade for their intended use. All consumables found to be contaminated are removed from use. The laboratory has a tracking system that incorporates the date of receipt, the date the container is opened, and the assigned expiration date of the chemical or standard. The procedures are documented in the individual laboratory Quality Assurance Manual.

Section B.9: Data Management

Internally, each agency will store all data in their own specific StarLIMS database (Laboratory Information Management system). Data will be transferred from the laboratories to the MPCA. Data will be stored in the MPCAs Environmental Quality and Information System (EQuIS) database.

Section B.9.1: Data Recording

Data and information collected in the field will be recorded in dedicated notebooks and forms. Data recording procedures to be followed by the laboratory are discussed in individual laboratory Quality Assurance Manual.

Section B.9.2: Data transformation

Data and field information is transformed in the MPCA offices. Procedures for data transformation by the laboratory are discussed in the laboratory Quality Assurance Manual. Data are input into various computer Projects for storage. The Projects utilized include Microsoft Access®, Excel® and Word®.

Section B.9.3: Data Transmittal

Data and field information are delivered to the MPCA using raw data notebooks and forms. Analytical data are submitted to the MPCA as final analytical reports. These reports have been reviewed and approved by the laboratory's technical, QA/QC, and project management staff. Data are then entered into a database by MPCA staff.

Section B.9.4: Data Rejection

Analytical data which does not meet the established QA/QC criteria defined in this QAPP is verified and either flagged as estimated or rejected. Field data is evaluated by the technical staff to ensure that it is compliant with the QAPP.

Section B.9.5: Data Tracking

MPCA staff contact the analytical laboratory on a regular basis regarding the status of sample analysis.

Section B.9.6: Data Storage and Retention

For MPCA, data storage and retention is dictated by Minnesota statute and department policy. Official laboratory records are managed using an inventory of records with a schedule establishing retention periods and disposal requirements.

Section C: Assessment and Oversight

Section C.1: Response Actions

Section C.1.1: Field Audit Project

An audit of the field sample collection activity may be made. This audit reviews equipment, personnel, training, field documentation (photographs, daily field logs, and checklists), and chain-of-custody records to ensure compliance to the QAPP. The results of the audits (and any identified corrective actions) are summarized in a report to management.

Section C.1.2: Laboratory Audits

Internal audits take place on an annual basis. These audits review the quality policies and implementation of the policies at the laboratory. The reports of these audits are sent to the laboratory manager and quality assurance officer for review and improvement in operations. The audit concentrates on the specific SOPs in each section, quality assurance practices, sample handling, documentation, and follow-up on prior audits. These audits are used by the laboratory to identify any problem in their operations before there is an effect to the data. All audits are documented and kept in the QA office. If problems occur or corrective action is initiated, the QAC from MPCA is contracted immediately for assistance in corrective actions. Copies of the internal audit findings (along with any required corrective actions) are submitted to the MPCA's QA Coordinator. As a result of the internal audits, the MPCA may audit at its discretion.

External audits of the laboratory may be performed by other accreditation bodies. Copies of the findings of these external audits (and any identified corrective action) are submitted to the MPCA's QA Coordinator. As a result of these external audits, the MPCA may audit at its discretion.

Section C.1.3: Performance Evaluation (PE) Studies

The laboratory analyzes Performance Evaluation Samples (PE Samples) which are blind samples prepared by external companies and shipped directly to the laboratory. The samples are logged in and analyzed as standard samples with the results being reported back to the independent company for scoring. The laboratory receives these scores and reports them to regulatory authorities (or states requiring PE samples for certification). Satisfactory performance must be maintained over the effective time of the QAPP. Copies of the results of the PE studies must be supplied to the MPCA's QA Coordinator.

Section C.2: Corrective Action/Reports to Management

For each analytical activity employed in this Project, the laboratory regularly tracks the overall quality assurance issues. When a quality control sample or QA issue is found to be out of control, Corrective Actions (CA) are implemented. Corrective action includes re-analysis of samples, re-sampling, flagging of data, or rejection of the data. MPCA is informed of any major CA that is performed on any Project sample.

Section C.2.1: MPCA Corrective Actions

The individual identifying a potential issue first documents the problem in the field notebook. The project manager who has final sign-off authority on any problem or issue tracks the problem. The project manager tracks all CA. The PM is responsible for identifying the problem, verifying proper documentation is written and implementing the correct action. The project manager will place final documentation into the site record. Any major CA involving the laboratory is tracked by the both the laboratory QAO and the MPCA project manager. The MPCA project manager has final sign-off authority on issues dealing with Project samples.

Section C.2.2: Laboratory Corrective Actions

Laboratories have a corrective actions system that is described in the laboratory QAM, if available. Generally, an individual involved in the analysis of the samples or review of the data discovers the problem. The problem is identified and documented. The documentation is important to allow tracking of the problem and ensure a proper solution is implemented. All analysts, QA staff, and managers/supervisors must agree to the solution to the problem. The QA staff will go back and verify that the solution corrected the problem. The documentation is archived with the client project folder.

Section C.2.3: Laboratory Reports

The laboratory sends a complete report to the MPCA that includes the following information:

a. A narrative discussing overall issues with the data (e.g. calibration, holding times, internal QC, etc.),
b. Extraction date,
c. Sampling date,
d. Analysis date,
e. Alphabetical list of compounds,
f. Reporting limits,
g. Method of analysis and extraction,
h. Signature of a laboratory officer,
i. Chain of custody,
j. Results of spike,
k. Spike duplicates,
l. Results of surrogate samples,
m. Blanks, and
n. Concentrations found of each analyte.

The laboratory report is given a final review by the laboratory project manager, then signed, and sent to the MPCA. Specific procedures used by the laboratory will be found in the QAM, if available.

Section C.2.4: Reports to Management

Reports to management will summarize the Project's sampling and analytical activities for the previous time period, the findings of the audits, any required corrective actions, the results of PE studies, any data quality problems (along with purposed solutions), any major changes in personnel, and an overall evaluation of the laboratory's quality assurance. The report is sent to all individuals identified in Section A.3.

Section D: Data Validation and Usability

Section D.1: Data, Reduction, Verification, and Validation

Section D.1.1: Data Reduction

In general, instrument response for the quantitative analytical procedures described in the laboratory SOPs is converted to concentrations or absolute amounts of analyte by use of a multipoint calibration curve which relates instrument response to the quantity of the analyte introduced to the instrument. The analyst reduces the raw data produced by the instrument using equations found in the laboratory SOP or QAM (if available). Technical expertise of the analyst is needed for evaluation of the data, reviews of the report produced from the raw data, and verification that the QC checks are within required limits (e.g. spikes, surrogates, blanks, duplicate spikes, etc.). The raw data and final report are submitted for verification.

Section D.1.2: Data Verification/Methods

The laboratory manager or designated experienced chemist verifies data is correct as reported. A manager reviews 100% of the raw data against the report (to verify data interpretation made by the chemist and that QC checks are correct) and makes sure no transposition errors were made. The laboratory QA Officer reviews a percentage of all reports to verify that data meets all requirements of the QAPP. The specific procedures to be followed by the laboratory are described in the laboratory QAM, if available. The flags used on the data will be consistent with those used by EPA for CLP data (J, R, U, B, etc.). The laboratory stores all raw data in their archives for five years. Raw data is available to MPCA staff as needed.

The MPCA Project staff does a data review when the analytical report is received. MPCA staff review data to verify all QC is acceptable, the project requirements are met (holding times and reporting limits), and that all required information is present in the report. The MPCA project manager reviews the data to ensure that all quality control requirements are met. The project manager also reviews the field duplicates, calculates the RPD, and compares the data to past data from the site to verify consistency. When all the data points have been reviewed, the project manager compares the data which is acceptable to the data which was planned for the site and verifies that the completion rate goal has been met. Any problems with the data or laboratory issues are immediately brought to the attention of the MPCA QAC who contacts the laboratory to assess the problems and find a solution. If the problem is particularly severe, a data audit or full laboratory audit may be conducted.

Section D.1.3: Data Validation/Methods

At least 10% of the data are validated by the MPCA QA Coordinator from the raw data. The validation process is consistent with the *National Functional Guidelines for Inorganic Data Review*. If any data problems are identified, more data packages are validated. If data does not meet the QAPP requirements and are judged to be unusable, the analyses are not paid for and the samples are re-collected.

Section D.2: Reconciliation with User Requirements

Data quality objectives have been met when a complete report (with all data qualifiers) has been provided to the MPCA Senior Management Team. The report includes any data issues identified by the laboratory or the MPCA. The report points out any limitations on the use of the data to decision makers.

Section D.3: References

1. U.S. Environmental Protection Agency, 2001. *EPA Requirements for Quality Assurance Project Plans (QA/R-5)*, EPA/240/B-01/003, Office of Environmental Information.

2. U.S. Environmental Protection Agency, 2002. *Guidance for Quality Assurance Project Plans (QA/G-5)*, EPA/240/R-02/009, Office of Environmental Information.

3. US EPA Contract Laboratory Project, January, 2010, *National Functional Guidelines for Inorganic Superfund Data Review, US*EPA-540-R-10-011, OSWER 9240.1-51.

Appendix A

Table of Acronyms

CA	Corrective Action
COC	Chain of Custody
CFR	Code of Federal Register
%D	Percent Difference
DQO	Data Quality Objectives
EPA	Environmental Protection Agency
FOC	Field Operations Center
LacCore/LRC	National Lacustrine Core Facility/Limnological Research Center
LIMS	Laboratory Information Management System
MDH	Minnesota Department of Health
MPCA	Minnesota Pollution Control Agency
MS	Matrix Spike
PE	Performance Evaluation (sample)
PI	Primary Investigator
PM	Project Manager
QAC	Quality Assurance Coordinator
QAO	Quality Assurance Officer
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
QMP	Quality Management Plan
RSD	Relative Standard Deviation
RPD	Relative Percent Difference
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SRF	Sample Receipt Form
SCWRS	St. Croix Watershed Research Station
UMN	University of Minnesota – Twin Cities
UMD	University of Minnesota - Duluth

Appendix B

MDH Environmental Laboratory QA Manuals

Quality Assurance Manual

for the

Environmental Laboratory Testing Units
Public Health Laboratory Division
Minnesota Department of Health
601 Robert Street North
P.O. Box 64899
St. Paul, Minnesota 55164-0899

Revision Record			
Rev. #	**Author/Revisor**	**Revision Date**	**Description of Change**
6	S. Drier	10/06/2006	Updated content due to change in lab location. New QA officer. Included revision history.
7	K. Peacock L. Liao	05/02/2007	Enhanced QC definitions (Section 2.0). Enhanced QC policies and procedures (Section 13.0). Minor edits throughout. Interim QA Officer.
8	Suzanne Skorich	09/22/2009	Enhanced QC definitions (Section 2.0). Organizational changes (Section 3.0). Enhanced chain-of-custody procedures (Section 8.0). Enhanced data reduction and validation procedures (Section 14.0). Enhanced system audits (Section 15.0). Updated certificates and forms (Section 17.0) Minor edits throughout.
9	Susan Wyatt	09/26/2011	Organizational changes (Section 3.0). Description of Promium Element LIMS Detail for system audits (Section 15.0). Minor edits throughout

CONTROLLED DISTRIBUTION

COPY #: **1 of 1**

ISSUED TO: **PHLD Intranet**

Quality Assurance Manual, Revision 9

Written/Revised By: /s/ Susan Wyatt, for quality manager Date: 09/29/2011
Susan Wyatt, Environmental Laboratory Accreditation Program Manager

Approved By: /s/ Paul Moyer Date: 09/29/2011
Paul Moyer, Environmental Laboratory Section Manager

Approved By: /s/ Joanne Bartkus Date: 09/29/2011
Joanne Bartkus, Public Health Laboratory Director

Table of Contents

Appendices

Table of Contents

SECTION 1.0: LIST OF ACRONYMS

The list of acronyms herein is limited to terms that are used in this Quality Assurance Manual outside of those listed in Section 2.0 "Definitions of QC Terms". The reader is directed to Section 2.0 for acronyms that correspond to various QC terms adopted by this laboratory and used in this Quality Assurance Manual.

CFR	Code of Federal Regulations
CWA	Clean Water Act
LIMS	Laboratory Information Management System
MDH	Minnesota Department of Health
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
OSHA	Occupation, Safety and Health Administration
PHLD	Public Health Laboratory Division
RCRA	Resource Conservation and Recovery Act
SDWA	Safe Drinking Water Act
USEPA	United States Environmental Protection Agency

SECTION 2.0: DEFINITIONS OF QC TERMS

The QC definitions and QC terms listed herein are standardized for use in this laboratory. Employees in this laboratory recognize that, in some cases, a particular USEPA-approved method and, in turn, a particular Standard Operating Procedure (SOP) may use different QC definitions and QC terms. In those situations, the QC in those particular SOPs supersedes the QC definitions and terms in this Quality Assurance Manual.

Acceptance Limits: A range within which specified measurement results must fall to be compliant. Acceptance limits may be mandatory, requiring corrective action if exceeded, or advisory, requiring that noncompliant data be flagged.

Accuracy: The degree of agreement between an observed value and an accepted reference value. Accuracy is a data quality indicator that includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations. Refer to the "Data Quality Section" of *Standard Methods*, for a more detailed explanation.

Aliquot: A representative portion of a sample taken for sample preparation and/or analysis and assumed to have been taken with negligible sampling error.

Analyte: The element, ion, compound, or other substance that an analytical procedure determines.

Analytical Run: The continuous analysis of one or more analytical batches using the same calibration.

Batch: Field and QC samples that are prepared and/or analyzed together. A **preparation batch** is a group of field and QC samples of the same matrix, prepared with the same process and personnel, using the same lot(s) of reagents. An **analytical batch** is composed of field and QC samples that are analyzed together as a group. An analytical batch can include prepared samples originating from various matrices provided that the matrices do not adversely affect other matrices, such as by carrying over to another sample matrix.

Bias: The systematic or persistent deviation of a measurement process which causes errors in one direction.

Blank Filter (BF): This applies to analyses where a filter is used to collect and retain the sample. The filter is processed and analyzed for the target analyte(s). Blank filters should be taken from the same lot as the sample filters and should be submitted by whoever provides the sample filters. The blank filter is used to determine background levels of the target analyte(s) that might be in or on the filters.

Blind Sample: A sample submitted for analysis to the laboratory with the true value(s) known only by the submitter. It is used to test the laboratory's proficiency in the execution of the measurement process.

Bottle Blank (BB) or Container Blank: A QC check of sample containers in which a blank matrix (reagent water, methanol, etc.) is added to selected containers and then processed and analyzed like any other sample. A representative number of bottle blanks, usually an amount equal to 1% of lots larger than 100 bottles, are tested from each lot of sample containers to determine whether container lots are free of target analyte(s) or interferences that may give positive results that are not from the actual sample(s). For further details see the "Bottle Blank procedures" for individual Laboratory Units.

Calibration: The process of quantifying an instrument's response to known values under specified conditions.

Calibration Blank: A zero standard that contains the reagents present in the calibration standards, but does not contain the target analyte(s). It can be used as a zero point standard in a calibration or for background subtraction.

Calibration Curve: The mathematical relationship between the known values, such as concentrations, of a series of calibration standards and the instrument response to a single analyte.

Calibration Range: The working range between (and including) the lowest and highest calibration standards, from which the value of unknown samples can be determined.

Calibration Standard: A substance or reference material used to calibrate an instrument.

Calibration Verification Standard (CVS): A standard, analyzed with an analysis batch that verifies the previously established calibration curve and confirms accurate analyte quantitation for all samples. The concentration of the CVS should be near the mid-point of the calibration curve. Also known as a Continuing Calibration Verification (CCV).

Certified Reference Material (CRM): A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation, and which is issued by a certifying body.

Chain of Custody (C of C): The procedures and records that document the possession and handling of samples from collection through disposal. See Section 8.0 of the Quality Assurance Manual for more details.

Chain-of-Custody Form: A record that documents the possession of the samples from the time of collection to receipt in the laboratory. This record generally includes: a unique Chain of Custody identification number; the number and types of containers; the mode of collection; collector; time of collection; preservation; and requested analyses.

Clean Water Act, CWA (Federal Water Pollution Control Act): The enabling legislation under 33 U.S.C. 1251 et seq., Public Law 92-50086 Stat. 816, that empowers USEPA to set discharge limitations, write discharge permits, monitor, and bring enforcement action for non-compliance.

Continuing Calibration Blank (CCB): A blank that is run with each batch of samples and at the end of the analytical run. The CCB may indicate contamination, carryover, baseline drift or other instrument or reagent changes occurring over the course of an analytical run that contributes to the value obtained for the quantity in the analytical procedure.

Continuing Calibration Verification (CCV): A standard, analyzed with an analysis batch that verifies the previously established calibration curve and confirms accurate analyte quantitation for all samples. The concentration of the CCV should be near the mid-point of the calibration curve. Also known as a Calibration Verification Standard (CVS).

Control Charts: Day-by-day or batch-by-batch plots of QC data, such as precision or accuracy, to visually monitor a process or analysis.

Control limits: The limits on a control chart such that, when data points fall outside them,

special causes of variation must be suspected. Control limits are usually defined as three standard deviations either side of the mean.

Corrective Action: The action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence.

Daily: Applies to the days during which the analytical process (including preparation of samples) is performed.

Data Quality Objectives (DQO): A statement of the appropriate type of data and overall level of uncertainty that a decision-maker is willing to accept in results derived from analytical data. DQOs are often expressed in terms of precision, accuracy, reliability, representativeness, and comparability.

Data Reduction: The process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useable form.

Data Validation: A process used to determine if data are accurate, complete, or meet specified criteria.

Detection Level or Detection Limit (DL): The lowest concentration or amount of the target analyte that can be identified measured and documented with confidence that the analyte concentration is not a false positive value.

Detection Level Study (DLS): The broad term for any study that determines the detection level for a given analyte or analysis. An MDL Study is one type of DLS.

Dissolved Analyte: The analyte in an aqueous sample that will pass through a 0.45 µm membrane filter prior to any sample preservation.

Duplicate: See field duplicates or laboratory duplicates.

Equipment Blank: A sample of analyte-free media which has been poured over or through the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

External Standard Calibration: The process of creating a mathematical relationship by directly comparing the concentrations of target analytes to their instrument responses in calibration standards. Samples are quantitated by using this mathematical relationship to calculate the concentrations of target analytes from the instrument responses to the same target analytes in samples.

Field Blank: An aliquot of reagent water or other appropriate blank matrix that is placed in a sample container in the field and treated as a sample in all respects, including exposure to sampling site conditions, equipment, storage, preservation (if necessary), and all analytical procedures. The purpose of the field blank is to determine if the field procedures or sample transporting procedures and environments could have contaminated the samples.

Field Duplicates (FD1 and FD2): Two separate samples collected in separate sample containers at the same time and place, under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Filter Blank (FB): For each batch of lab filtered or field filtered samples, reagent water is passed through one or more unused 0.45 µm filter(s) and the filtrate from each is collected. The filtrate is treated like all other dissolved samples in the batch. Analysis of the filter blank will reveal contamination from the filter or filtration process.

Holding Time (Maximum Allowable Holding Time): The maximum time that a sample may be held prior to preparation and/or analysis and still be considered valid or not compromised.

Initial Demonstration of Capability (IDC): A procedure by which an analytical team must demonstrate acceptable precision, accuracy, sensitivity, and specificity for the analysis prior to its initial use. For additional information see the "Policy and Procedure for Initial Demonstration of Capability Study" in Appendix 10, p. 57-58, of the QA Manual.

Intermediate Standard: A solution made up from the stock standard solution and diluted as necessary to prepare working standard solutions.

Internal Standard (IS): A constant amount of non-target analyte that is added to all samples, blanks, and standards. The internal standard calibration process may be used to calculate the concentration of target analyte(s) and surrogate(s) that are components of the sample or solution. The internal standard should not be present in the original test sample at interfering levels and should behave similarly to the target analyte(s). Ideally, the retention times of internal standards should be near the retention times of the associated target analytes. See individual SOPs for additional criteria applicable to the use of internal standards.

Internal Standard Calibration: The process of creating a mathematical relationship by comparing the instrument response of a target analyte in a calibration standard to the response of an internal standard added to the calibration standard. The relative response factor (RRF) created by this process is used to calculate the concentration of the target analyte in other samples to which the internal standard has also been added. Internal standards are used to correct for routine variations in instrument response, extraction efficiency, and/or for variations in the exact

volumes of the samples or sample extracts. The internal standard(s) is added to all samples, blanks and standards at a constant amount, should not be present in the original test samples in interfering amounts, and should behave similarly to the target analyte.

Laboratory Control Sample (LCS): An aliquot of reagent water or other blank matrix, known to be free of interfering amounts of target analytes or other interferences, to which known quantities of the target analytes are added in the laboratory. The spiking solution for the LCS should be prepared from the same source as the calibration standards. It is prepared and analyzed exactly like a sample. Its purpose is to verify that the procedure is in control and that the laboratory is capable of making accurate measurements. A LCS is also known as a Laboratory Fortified Blank (LFB).

Laboratory Control Sample Duplicate (LCSD): A second aliquot of reagent water or other blank matrix, known to be free of interfering amounts of target analytes or other interferences, to which known quantities of the target analytes are added in the laboratory. The LCSD is prepared the same as the LCS. The LCS and LCSD are treated exactly as samples throughout the laboratory procedure. The percent recoveries for the target analytes are a measure of accuracy while the Relative Percent Difference (RPD) between the LCS/LCSD measures is a measure of precision. It is also known as a Laboratory Fortified Blank Duplicate (LFBD).

Laboratory Duplicates (LD1 and LD2): Two aliquots taken from a single sample container in the laboratory and analyzed separately using identical procedures. Analysis of LD1 and LD2 indicates precision associated with laboratory procedures for a specific sample matrix, but not with sample collection, preservation, or storage procedures.

Laboratory Fortified Blank (LFB): See Laboratory Control Sample (LCS).

Laboratory Fortified Blank Duplicate (LFBD): See Laboratory Control Sample Duplicate (LCSD).

Laboratory Fortified Matrix (LFM): See Matrix Spike (MS).

Laboratory Fortified Matrix Duplicate (LFMD): See Matrix Spike Duplicate (MSD).

Laboratory Reagent Blank (LRB): See Method Blank (MB).

Linear Calibration Range (LCR): The concentration range, as determined by the analysis of calibration standards, over which the calibration curve is linear.

Linear Dynamic Range (LDR): The concentration range over which the instrument response is linear. The LDR may extend beyond the calibration range. A LDR study is required to confirm the validity of reporting data beyond the calibration range.

Material Safety Data Sheet (MSDS): Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire hazard, and reactivity including storage, spill, and handling precautions.

Matrix: The predominant material of the sample to be analyzed. Matrices include, but are not limited to: air, drinking water, non-potable water, sewage sludge, solids, and chemical materials.

Matrix Spike (MS): An aliquot of a field sample to which known quantities of the target analytes are added in the laboratory prior to sample preparation and analysis. The spiking solution for the MS should be prepared from the same source as the calibration standards. The MS is prepared and analyzed exactly like a sample. The background concentrations of the analytes in the sample matrix must be determined in an unspiked aliquot of sample and subtracted from the MS concentrations. The purpose of the MS is to determine whether the sample matrix contributes bias to the analytical results. MS is the same as Laboratory Fortified Matrix (LFM).

Matrix Spike Duplicate (MSD): A second aliquot of sample to which known quantities of the target analytes are added in the laboratory prior to sample preparation and analysis. The MSD is treated exactly the same as the MS. The percent recoveries for the target analytes are a measure of accuracy while the Relative Percent Difference (RPD) between the MS/MSD is a measure of precision. The MSD is the same as Laboratory Fortified Matrix Duplicate (LFMD).

Maximum Contaminant Level (MCL): The maximum permissible level of a contaminant in water which is delivered to the free flowing outlet of the ultimate user of a public water system. See 40 CFR Part 141.2.

Maximum Contaminant Level Goal (MCLG): The maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. Maximum contaminant level goals are nonenforceable health goals. See 40 CFR Part 141.2.

May: Denotes a permitted, but not a required action.

Method: A scientific technique for performing a specific measurement as published by a recognized authority.

Method Blank (MB): An aliquot of reagent water or other blank matrix known to be free of interfering amounts of target analytes or other interferences. The MB is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, acids, internal standards and surrogates that are used with samples. The Method Blank is used to determine if target analytes or other interferences are present in the laboratory environment, reagents or

apparatus that may give false positive results. The MB is also known as a Laboratory Reagent Blank (LRB), laboratory blank, laboratory method blank, reagent blank, or preparation blank.

Method Detection Limit (MDL): The minimum concentration of an analyte that can be measured and reported with 99% confidence that the concentration is greater than zero. The MDL is determined from multiple analysis of samples in a given matrix containing the analyte. See 40 CFR 136 App. B for the procedure used to determine the MDL.

Minimum Reporting Level (MRL): The lowest concentration for which future recovery is predicted to fall, with high confidence (99%), between 50 and 150%. For additional information see the UCMR2 Laboratory Approval Manual, version 2.0, October, 2006.

Monthly: Applies to those months during which the analysis is performed.

Must: Describes an action, activity or procedural step that is required. Must is synonymous with shall.

National Environmental Laboratory Accreditation Conference (NELAC): A voluntary association of state and federal agencies whose purpose is to establish and promote mutually acceptable performance standards for the operation of environmental laboratories. The current name for this association is The NELAC Institute (TNI).

National Environmental Laboratory Accreditation Program (NELAP): The overall National Environmental Laboratory Accreditation Program of which NELAC is a part.

Percent Recovery: A measure of the accuracy of a measurement in a given matrix. A known amount of analyte is added to a blank or sample and the concentration found is divided by the concentration of the spike. The result is multiplied by 100 to express the value in percent. The formula is as follows:

$$\% \text{ Recovery} = \frac{C_s - C_u}{C_t} \times 100$$

where:
C_s = Measured concentration of the spiked sample aliquot or blank
C_u = Measured concentration of the unspiked sample aliquot (Use 0 for an LFB or LCS)
C_t = True value of the concentration of the spike added to the sample or blank

Percent Relative Standard Deviation (%RSD): A measurement of the precision of a series of replicate analyses where the Standard Deviation (S) of the replicates is expressed as a percent of the mean (X) value. To calculate:

$$\% \text{ RSD} = \frac{S}{X} \times 100$$

where:

S = Standard Deviation
X = Mean value

Post Digestion Spike (PDS): An aliquot of a sample to which known quantities of the target analytes are added after digestion to determine matrix effects.

Precision: The measure of mutual agreement among individual measurements of replicate samples under similar conditions. The most commonly used estimates of precision are standard deviation (S), percent relative standard deviation (%RSD), and relative percent difference (RPD).

Preservation: Chemical or physical treatment of the sample to retard the chemical and biological changes that occur after the sample was collected from the parent source.

Procedural Standard Calibration: A calibration method in which aqueous calibration standards are prepared and processed (e.g., extracted, and/or derivatized) in exactly the same manner as the samples. All steps in the process from addition of sampling preservatives through instrumental analyses are included in the calibration. Using procedural standard calibration compensates for any inefficiencies in the processing procedure.

Proficiency Testing (PT): A procedure for evaluating an analyst's or laboratory's performance relative to a given set of criteria through the analysis of unknown samples provided by an external source.

Proficiency Test Sample: A sample obtained from an approved provider to evaluate the ability of the laboratory to produce an analytical test result meeting the definition of acceptable performance. The concentration of the analyte(s) in the sample is unknown to the laboratory at the time of analysis.

Quality Assurance (QA): An integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence.

Quality Assurance Manual (QAM): A document stating the management policies, objectives, principles, organizational structure and authority, responsibilities, accountability, and implementation of a laboratory or other organization, to ensure the quality and the utility of its product to its users.

Quality Assurance Plan (QAP): A comprehensive plan detailing the specific quality assurance

required of the Laboratory to adequately fulfill the data requirements of a program.

Quality Assurance Project Plan (QAPP): A formal document describing the detailed quality control procedures by which the quality requirements defined for the data and decisions pertaining to a specific project are to be achieved.

Quality Control (QC): The routine technical activities that give insight into the precision and accuracy of analysis results.

Quality Control Sample (QCS): A standard containing target analytes of known concentrations which is used to verify the initial calibration. The QCS is obtained from a source different from the source of the calibration standards or from a different lot if a second source is not available.

Quality System: A set of policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC.

Raw Data: Describes any original factual information from a measurement activity or study recorded in laboratory notebooks, worksheets, records, memoranda, notes, or photo copies thereof, that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, computer printouts, magnetic media, and recorded data from automated instruments. After processing, some raw data are passed to the laboratory's database (Laboratory Information Management System or LIMS) which enables the data to become compiled into reports or to become accessible for further analysis or processing.

Reagent Blank (RB): See Method Blank.

Reagent Water: Water known to be free of interfering amounts of target analytes or other interferences. Individual SOPs may have additional requirements.

Reference Method: A test method issued by a nationally recognized organization from which the laboratory's analytical Standard Operating Procedure (SOP) is derived.

Relative Percent Difference (RPD): A measure of precision between two values, such as analysis of duplicates, MS/MSD, or LCS/LCSD. It is calculated with the formula below:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:

C1 = Measured concentration of the first sample aliquot.
C2 = Measured concentration of the second sample aliquot.

OR more simply:

$$RPD = \frac{\text{Difference between duplicates}}{\text{Mean of duplicates}} \times 100$$

Relative Standard Deviation (RSD): See percent relative standard deviation.

Replicate: Two or more aliquots of a sample analyzed independently and used to determine precision. In some analytical methods, the reported value is an average of all of the replicate analyses.

Report Level (RL): The lowest concentration of a target analyte that can be reliably measured, within specified limits of precision and accuracy, during routine laboratory operating conditions. RL is also known as reporting level, report limit, reporting limit and quantitation level.

Report Level Verification (RLV): A procedure that determines whether the established report level is valid for a target analyte within an analysis and/or analytical run. This procedure is performed by the analysis of a standard at or below the report level. For further details, see the "Policy and Procedure for Report Level Verification" in the Appendices to the QA Manual.

Requirement: Denotes a mandatory specification, often designated by the terms "shall" or "must".

Resource Conservation and Recovery Act (RCRA): The enabling legislation under 42 USC 321 et seq. (1976), that gives USEPA the authority to control hazardous waste from the "cradle-to-grave", including its generation, transportation, treatment, storage, and disposal.

Run: See analytical run.

Safe Drinking Water Act (SDWA): The enabling legislation, 42 USC 300f et seq. (1974), (Public Law 93-523), that requires the USEPA to protect the quality of drinking water in the U.S. by setting maximum allowable contaminant levels, monitoring, and enforcing violations.

Sample: A representative portion of material (water, soil, etc.) collected for analysis in the laboratory. A sample must be uniquely identified. When the sample is further prepared by subdividing, mixing, or grinding, or a combination of these operations, the result is a test sample.

When no preparation of the sample is required, the sample is the test sample. An aliquot is removed from the test sample for the performance of the test or for analysis.

Shall: Denotes a mandatory requirement. Shall is synonymous with must.

Should: Denotes a recommended but not required action.

Spike: A known quantity of target analyte(s) added to a blank or sample aliquot. This QC standard is used to determine recovery or for other quality control purposes. See MS or LCS.

Spiking solution: A solution containing a known concentration of target analyte(s) used to fortify a blank or sample for quality control purposes.

Standard: A solution or other material with a known value that is used in the laboratory to perform calibrations or QC checks.

Standard Curve: See calibration curve.

Standard Reference Material (SRM): A certified reference material produced by the U.S. National Institute of Standards and Technology (NIST) and characterized for absolute content, independent of any analytical method.

Standard Operating Procedure (SOP): A written document that details the techniques and procedures of an operation, analysis, and/or action and is officially approved as the method for performing certain routine functions. The SOP is written to ensure the generation of usable and consistent results.

Stock Standard: A concentrate containing one or more target analytes that is purchased from a commercial source or prepared in the laboratory. The stock standard is used to prepare intermediate standards, and calibration standards.

Surrogate: A non-target analyte added to samples, blanks, and standards before sample preparation. The surrogate is added at a known concentration and is used to determine the efficiency of the sample preparation process. Surrogates should possess chemical properties similar to those of the target analytes, but should not be present in the original test sample.

Target Analyte: The analyte in a given matrix that is determined by an analytical procedure.

Test Sample: The prepared sample from which test portions are removed for analysis.

Trip Blank: An aliquot of reagent water or other appropriate blank matrix taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to

document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

Unregulated Contaminants: Contaminants that require monitoring under the National Primary Drinking Water Regulations but have no MCL.

Weekly: Applies to the weeks during which the analytical process (including preparation of samples) is performed.

SECTION 3.0: GENERAL LABORATORY INFORMATION AND POLICIES

A. Organization

The Environmental Laboratory is located within the Minnesota Department of Health's Public Health Laboratory Division (PHLD). In addition to the Environmental Laboratory Section, division management oversees the Environmental Laboratory Accreditation Program, the Clinical Laboratory Section, and the Newborn Screening Section. The Technical Services Unit and Clerical Services Unit are directly supervised by the Assistant Division Director. The PHLD organizational chart, focusing on the environmental testing units, is presented in Appendix 1, p. 42.

The Environmental Laboratory Section supports public health and environmental protection functions of state government by performing chemical, bacteriological and radiological analyses of environmental samples including drinking water, surface water, waste water, sediment, air, fish, soil and hazardous waste. The laboratory provides these testing services for programs in the Environmental Health Division at the Minnesota Department of Health, for the Minnesota Pollution Control Agency, the Minnesota Department of Transportation, the Minnesota Department of Labor and Industry, and various agencies of local government. The MDH Environmental Laboratory Handbook (http://fyi.health.state.mn.us/phl/environmental/index.html) lists current partners and clients along with established LIMS project codes. The laboratory maintains the capability to respond to chemical and radiological emergencies within Minnesota and with limited abilities to analyze clinical specimens. The laboratory also develops new analytical methods and provides technical training and consultation at the request of its clients. The Environmental Laboratory ensures that testing capacity is available to support the public health and environmental protection objectives of the state.

The MDH Environmental Laboratory Section is organized into 4 units. Three of these units, *viz.* the Inorganic Chemistry Unit, the Organic Chemistry Unit, and the Operations Unit comprise the environmental testing units. They include the following technical areas: General Chemistry, Metals Chemistry, Organic Chemistry, Radiation Chemistry, Water Microbiology as well as administrative functions carried out in the Operations

Unit. Additional administrative and technical support is provided by the Sample Receiving Unit.

B. Facility Description and Location

The Public Health Laboratory Division is located at 601 Robert Street North, St. Paul, Minnesota. The laboratories are co-located with the Minnesota Department of Agriculture. The two departments operate under separate quality systems, analytical staff, and management. The MDA/MDH laboratory building measures 176,500 gross square feet; three levels are occupied, and the fourth level houses the air handling systems. Approximately 60% of the building's space is utilized by the PHLD.

The building ventilation system includes a state-of-the-art heat-recovery wheel to save on long-term energy costs and air filtration. The building has 100% outside air running through the labs with no recirculation. In addition, the air in the metals clean room area is HEPA-filtered. The metals clean room, the routine metals area, and the radiation chemistry area are equipped with polypropylene hoods to protect the integrity of the hood surfaces and reduce risk of contamination from corrosion. Ventilation hoods have digital sensors (monitoring for image detection as well as movement) to automatically adjust for appropriate airflow. The automated system reduces the amount of heat loss through the hoods while protecting the health and safety of the workers.

C. Building Security

The MDA/MDH Laboratory building is a locked, secure area, and it is not open to the public. Visitors must register at the Orville Freeman Office Building reception desk and receive one of three types of security badges:

1) "Lab Visitor" badges provide access to the front door and the atrium's turnstiles during regular business hours. These visitors then have access to the elevators and conference rooms on the 2nd and 3rd floors.

2) "Lab Staff" badges provide access to the general lab spaces throughout our building and general spaces in the Freeman Building during regular business hours.

3) "Contractor" badges provide access to all of the general lab spaces throughout our building and general spaces in the Freeman Building. The "Contractor" badges also provide access to the engineering spaces in both buildings.

Visitors must be escorted by an authorized employee while in the laboratory facility.

SECTION 4.0: POLICIES

A. Quality Assurance Policy

Laboratory staff members provide quality data and services to clients, according to their needs. The laboratory management team considers quality to be an ongoing process of improvement and an integral part of the laboratory's testing and support operations. To support the quality goals, the laboratory management team ensures that adequate facilities, supplies, staffing, and supervision are available to perform the testing required. The laboratory's management team ensures that quality measures are documented and data are stored and disseminated in a manner that allows access to public data while protecting client confidentiality. This manual and its related procedures specify the activities performed to achieve the quality goals of the laboratory and its clients.

B. Ethics Policy

Minnesota Statutes, 43A.38 lists the required code of conduct for all state employees. This statute defines policies that relate to gifts and favors, use of confidential information, use of state property, and declared or potential conflicts of interest. The full text of the Minnesota Statute is available online at: http://www.revisor.leg.state.mn.us/stats/43A/38.html.

C. Data Practices Policies

Minnesota Statutes, Chapter 13, Government Data Practices, describe the regulations that govern the collection, storage, maintenance, dissemination and access to government data in government entities. They presume that government data are public and are accessible to the public for both inspection and copying unless there is federal law, state statute, or a temporary classification of data that provides that certain data are not public. The full text of the Minnesota Statutes, Chapter 13, and other MDH policies regarding data practices are online at: http://fyi.health.state.mn.us/datapractices/index.html

D. Computer Security Policy *see Section 6.0 of this manual.*

E. Corrective Action Policy *see Section 15.0 of this manual.*

SECTION 5.0: PERSONNEL

A. Positions and Responsibilities

Public Health Laboratory Division Director: sets policies for the operation and management of the Public Health Laboratory Division.

Environmental Laboratory Management Team: authorizes training and development for

laboratory personnel, approves staffing plans, and has overall responsibility for the administration of the Environmental Laboratory. Management includes laboratory operations and project management functions which have responsibility for ensuring that analyses are conducted according to program requirements, establishing contracts, compiling and distributing reports and preparing budgets.

Environmental Laboratory Quality Assurance Officer: ensures that the quality of the data generated by the laboratory meets the goals of the laboratory's policies, maintains quality assurance records, conducts internal audits, requires and tracks corrective actions and responds to requests for corrective actions due to deficiencies noted during external audits by the USEPA, clients, or proficiency testing studies.

Environmental Laboratory Testing Unit Supervisors: are responsible for supervision of analysts. They also ensure that testing procedures are current and accurate, adequate training is provided and documented for all analysts, required quality control practices are performed, analysts perform timely review of QC results, data are appropriately reviewed for errors in calculations or transcriptions, and all out-of-specification situations are resolved and documented according to QA procedures.

B. Training

1) General Employee Training (for all staff)

New employees are asked to participate in a six hour "New Employee Orientation" training, hosted by the department training coordinator, within the first three months of their employment. This training provides information about functions and policies of MDH and the State of Minnesota.

All employees in the environmental testing units are required to read, understand and agree to comply with the contents of the laboratory's Quality Assurance Manual and the specific referenced policies and procedures that are pertinent to the individual analyst. These include pertinent sections of the references listed in Section 16.0, "References", pp. 36-37, pertinent appendices included in this Quality Assurance Manual, and pertinent Standard Operating Procedures (SOPs). Copies of the completed Quality Assurance Manual Agreement Form are kept in the training files for all employees. The text of the agreement is as follows:

Quality Assurance Manual Agreement

As an employee in an environmental testing unit of the MDH Public Health Laboratory Division, I have read and understood the contents of the currently approved Quality Assurance Manual. I have also read and

understood the referenced policies and procedures that are pertinent to my analytical assignments. I understand that I am expected to comply with the Quality Assurance Manual and the referenced policies and procedures.

The professional development of staff is a vital component of fiscal planning throughout the department. Laboratory management encourages memberships in professional organizations. The department maintains membership in the American Water Works Association and the Association of Public Health Laboratories. Laboratory staff maintains membership in associations related to their technical disciplines such as the Minnesota Chromatography Forum, the American Chemical Society, the American Society for Microbiology, the American Society for Mass Spectrometry, and the American Water Works Association.

Additional educational opportunities at colleges or universities are encouraged and may be paid in-part or in-full at the discretion of the unit supervisor and division management. Supervisors may recommend attendance based on the applicability of the course to current duties of the applicant or based on the course's applicability to future goals of the division or department. In some cases, release time from work to attend courses may be permitted in addition to or in lieu of registration payment.

The PHLD Health and Safety Officers provide safety training to all new PHLD employees. They also conduct safety and Right-to-Know training annually for all lab employees. Employees are expected to be familiar with the documents posted on the PHLD Safety website: http://fyi.health.state.mn.us/phl/safety/index.html. These include the Chemical Hygiene Plan, the Hazardous Waste Manual, Radioactive Waste Management, First Report of Injury Form, and Emergency Procedures. Safety training related to the specific assignments of the employee is provided by the supervisor, in consultation with the PHLD Health and Safety Officers. The training meets the requirements of OSHA's Hazard Communication Program (29 CFR 1910.1200).

In addition to courses required of all division employees, supervisors and managers must attend core management training courses offered by the Minnesota Department of Employee Relations (DOER). Both MDH and DOER publish training bulletins to inform employees of a wide variety of course offerings.

2) Radiation Safety Training (for selected staff)

Initial radiation safety training and annual refresher training are required for staff who will work with or in the vicinity of radioactive materials. Training for the selected staff covers radiation hazards, appropriate precautions, and emergency procedures. For staff who will handle radioactive materials directly, the training also includes special procedures related to their specific laboratory use of radioactive material.

Training is presented through lectures, demonstrations, and self-directed media. Participants are required to sign an attendance log or a statement acknowledging that they have completed the training requirement. Training records are maintained by the Radiation Safety Officer. The laboratory's Radiation Emergency Plan is available to all employees on the PHLD Safety website: http://fyi.health.state.mn.us/phl/safety/index.html

3) Initial Demonstration of Capability (for laboratory analysts)

Analysts who are learning analytical standard operating procedures (SOPs) receive technical training from the supervisor, the lead worker, or an experienced analyst for all assigned procedures. Initially, the trainer demonstrates and explains the process to the trainee. After observing the trainer, the trainee performs the analysis while the trainer observes. The analyst (trainee), experienced analyst (trainer), and supervisor document the demonstration of capability and submit a completed training record to the Quality Assurance Officer. Appendix 2, p. 43, displays the "Training Record for an Individual Standard Operating Procedure". [Note: Section 13.0, "Quality Control", pp, 32-33, describes the policies, procedures, and worksheets germane to these aspects of the analysts' training.]

4) Ongoing Demonstration of Capability (for laboratory analysts)

On an annual basis, laboratory analysts must demonstrate their continued capability to perform the assigned procedures. Acceptable demonstrations of capability may include any of the following: successful analysis of a series of laboratory control samples with results statistically comparable to those of a trained analyst, successful completion of a proficiency testing study, or successful repetition of the initial demonstration of capability. The laboratory staff must verify the demonstration of capability option selected meets method-specific or client requirements.

Training of employees in the technical areas may require participation at conferences, workshops, and courses. Subscriptions to scientific journals and participation in analytical laboratory organizations assist analysts in maintaining knowledge of the latest technology. On-site training conducted by manufacturers on the operation of their instruments is common. Appendix 3, p. 44, contains a copy of the "Record of Personnel Education and Training", which is completed by each analyst and filed in the Quality Assurance Office.

SECTION 6.0: INFORMATION TECHNOLOGY

A. Specifications for the Laboratory Information Management System (LIMS)

The PHLD uses the Promium LIMS product Element, which is a Client Server Application running against Oracle Database 10.2.0.4. Backup of data is accomplished using Commvault backup software where tapes are cycled weekly to an offsite vendor on a 2-week rotating

system.

B. Computer Security

All laboratory employees must follow the MDH Information Resources Security Policy, http://fyi.health.state.mn.us/comm/irm/sc/infosec/se010122securitypolicy.pdf. This policy is designed to counter risks to information security that are internal and external to the organization. Such risks include loss of privacy (reading of information by unauthorized persons), loss of data (corruption or erasure of information), and loss of service (filling of data storage space, use of computational resources, denial of network access). Although intruders on security systems and computer viruses are the most highly publicized security breaches, many computer security surveys show that the greater risk is from individuals working inside an organization. In order to design cost-effective security policies and plans, the threats to the security of the information resources of an organization must be analyzed in terms of how they affect the availability, confidentiality, and integrity of those resources.

The departmental security policy was developed by the Information Resources Management (IRM) Steering Committee, through its Security Subcommittee. The Security Subcommittee is a cross-divisional group of managers with budget and policy authority and IT staff with technical expertise. The security policy was created with input from individuals throughout the department who have responsibilities for the security of information resources.

C. Additional Software

The laboratory uses a variety of software programs for data production, reduction, verification and validation. In addition to routine office software (MS Office Professional), the laboratory uses instrument software that varies according to the vendor and the intended purpose. The laboratory uses validated software as supplied, installed and maintained by the vendor.

SECTION 7.0: SAMPLING

The laboratory does not perform its own sampling; nonetheless, the laboratory and the sample accessioning/receiving area do provide guidance to field personnel for proper submission of samples to the laboratory. The laboratory's clients, or their contracted staff or volunteers, are responsible for training collectors, collecting samples, and delivering samples to the laboratory. The laboratory does not routinely accept samples collected by the general public.

Instructions on the proper submission of samples (bottle type, preservative, labeling, and forms) are included in various sample receiving area procedures and in the MDH Environmental Laboratory Handbook. The handbook is posted at both the internal website:

http://fyi.health.state.mn.us/phl/environmental/index.html and the external website: http://www.health.state.mn.us/divs/phl/environmental/handbook/internet/envhandbook.html

SECTION 8.0: SAMPLE CUSTODY, HANDLING AND TRACKING

A. Receiving Hours

The laboratory accepts samples at the loading dock area between the hours of 7 a.m. and 6 p.m. (or from 8 a.m. to 4:30 p.m. for civil or criminal chain-of-custody samples) Monday through Friday. The laboratory recommends pre-arranged drop-off schedules for all samples requiring special receiving conditions (*e.g.* civil or criminal chain-of-custody samples) and sample deliveries outside regular hours.

B. Sample Acceptance/Rejection Criteria

For all samples, the person delivering the samples submits the appropriate "sample analysis request forms" (a.k.a. chain-of-custody forms). Information to be included on the form includes the appropriate analysis and project codes, the sample collection dates and times, the date of delivery to the laboratory, the field numbers, the name or identification number of the site from which the samples were collected, and whether the samples were split with another laboratory. Examples of "sample analysis request forms" (a.k.a. chain-of-custody forms) are provided in Appendices 4 and 5, pp. 45-47.

After the sample bottles have been examined and the sample receipt custodian is satisfied the samples have been collected in appropriate containers, shipped properly, and arrived in acceptable condition, the samples are accepted. Samples accepted by the sample receipt custodian are logged into the LIMS. With samples that require thermal preservation, the sample receipt custodian records the temperature of a representative sample on the "sample analysis request form." The sample receipt custodian assigns sample identification numbers, documents these sample identification numbers on the "sample analysis request form", and attaches the sample identification numbers (using LIMS-generated labels) to the corresponding sample containers.

The LIMS automatically evaluates information for received samples to determine if holding times have been exceeded. If samples were received past the holding time for the tests to be conducted, the LIMS generates a message via electronic mail to the authorized recipient for the project code requested. All issues are referred to the Operations Unit for resolution. The electronic message requests a reply from the recipient for permission to reject the sample or for permission to analyze the sample and report the associated data with qualifiers.

For some projects, the client's project manager has pre-approved the laboratory to take specific actions. These exemptions from the notification process are programmed in the LIMS as business rules. When samples are received and do not meet the laboratory's

acceptance criteria, the LIMS determines whether a business rule applies. If a business rule applies, the LIMS will allow the sample receipt custodian to accept or reject the samples and generate an electronic message with no need for a response. Approval for these conditions has already been given by the client. In those instances, the LIMS will qualify the data on the final report without further interaction from the operations unit or laboratory staff.

If the custodian determines that samples do not meet receipt requirements, sample receiving personnel enter into the LIMS the condition of the samples or sample containers and the reason for rejection. The most common errors in submission or reasons for rejection of samples are available as drop-down options in the LIMS; nonetheless, the sample receiving staff has the option to enter free text for particular conditions not otherwise identified. When problems are identified by the sample receiving staff and entered into the LIMS, the sample receiving personnel initiate requests for resolution of discrepancies according to a procedure similar to those for messages sent for holding time issues as explained above.

C. Civil or Criminal Chain-of-Custody Procedures

Due to the evidentiary nature of samples collected during enforcement investigations, sample possession must be traceable from the time samples are collected until they are disposed and until their derived data are used for enforcement purposes or are introduced as evidence in legal proceedings. The laboratory uses civil or criminal chain-of-custody procedures to maintain a record that tracks each sample and each individual responsible for sample collection, receipt, analysis, and disposal. An example of a chain-of-custody form associated with receipt of samples involved in enforcement actions is provided in Appendix 5, p. 47. The laboratory maintains a bound, civil or criminal chain-of-custody logbook to internally track samples that are associated with enforcement activities. A page from the civil or criminal chain-of-custody logbook is contained in Appendix 6, p. 48. The laboratory's civil or criminal chain-of-custody procedure is described below.

The laboratory considers a sample "in custody" if the sample is: in a person's actual possession; in view after being in a person's physical possession; or in a person's possession and that person placed the sample in a secured area.

For custody samples, the samples and submission forms are hand-delivered or sent in a sealed shipment container and are received at the laboratory by a designated sample receipt custodian. If a tag was used to seal the shipment container, the custodian examines the seal tag to check for tampering. The custodian breaks the intact seal and opens the container to verify that the tag number written on the custody form matches the number on the container seal.

If the samples are being hand delivered by someone other than the person who signed for custody of the samples on the chain-of-custody form or the tag on the sealed shipment

container is not intact, the sample receipt custodian does not accept the samples. The sample receipt custodian records the information in the comments section on the chain-of-custody form and notifies the Quality Assurance Officer or a unit supervisor. The sample receipt custodian notifies the client of the discrepancies and obtains further instructions.

The custodian examines the samples to determine that they meet laboratory requirements, that no damage to the sample bottles has occurred, and that the sample seal tape, if used on the bottles, is still intact. The custodian compares the field numbers assigned to the samples by the sampling team leader to those recorded on the custody form. If anything is not in order, the custodian records information in the comments section on the chain-of-custody form and notifies the client.

Entries into all records must be written legibly and erasures or marking shall not obliterate entries in records. All corrections must be made by one line marked through the error leaving the original record visible. The individual making the correction must sign or initial and date the correction.

The chain-of-custody form, which is completed in triplicate, is distributed as follows: the original is kept by the laboratory in a three-ring binder, the yellow copy is attached to the "sample analysis request form" and returned to the client upon completion of the analytical work, and the pink copy is given to the sampler upon relinquishing custody of the samples.

When the samples have been properly accepted and logged into the LIMS, the sample receipt custodian delivers the samples and any chain-of-custody forms to the laboratory. Information concerning the identification and transfer of civil or criminal chain-of-custody samples is recorded in a bound log book, and the samples are placed in a designated, secure storage area. While access to general laboratory areas is restricted to authorized personnel, the civil or criminal chain-of-custody samples are further protected in a secure location with access restricted to a smaller number of authorized personnel.

Additional information entered into the chain-of-custody logbook includes chain-of-custody record number, site or I.D. number, matrix, sample collector, all types of bottles received, and whether the samples are involved in a civil or criminal investigation.

For the analysis of samples associated with criminal investigations, only designated analysts receive the samples, thereby limiting the number of people handling the samples.

The analysts are responsible for the care and custody of the samples once they are in their possession. Analysts should be prepared to testify that the samples were in their possession and view, or locked in a secure area, from the time they received the samples until they returned the samples to be placed in the appropriate secured storage area. Aliquots of the original samples undergoing analysis remain within the secured areas of the laboratory at all

times.

Upon completion of the analytical work, the samples are returned to the secured storage area. The date and time of the return are recorded in the chain-of-custody log along with the initials of the analyst. In the event that the entire sample was used for the analysis, the empty sample container is returned to the secured storage area and the date and time of the return are recorded with the initials of the analyst.

Once all analyses are completed, the original sample containers are stored in the secured storage area until the disposal of the samples has been approved by the client. The laboratory provides the client with a list of chain-of-custody samples which are ready for disposal on a quarterly basis. Upon client approval, the laboratory properly discards the samples. The dates of disposal of such samples are recorded in the chain-of-custody log book.

D. Data Records for Custody Samples

Upon the completion of the analytical work and computation of the data, a report is generated. The analytical results are reviewed by appropriate laboratory staff. Once the data have been reviewed and approved for release to the client, the data packages are prepared. Data generated from the analysis of any sample collected by the client shall not be released to any outside interested party unless the client has provided the laboratory with prior written approval.

The data package is sent to the client's designated staff person for review. The data package includes: the original "sample analysis request form"; final results recorded on the form or supplied on attachments; the yellow copy of the chain-of-custody form; and any corresponding quality control data requested by the client. The laboratory maintains complete copies of all laboratory records.

E. Sample Custodians

A member of the Environmental Laboratory Management Team is designated as the custody coordinator. The custody coordinator maintains a list of sample custodians and ensures proper training and appropriate access to custody areas. The following positions are designated sample custodians for the laboratory: sample receiving personnel, quality assurance officer, and unit supervisors or their designees.

F. Additional Instruction

Additional guidelines for sample collection, storage and delivery for civil or criminal chain-of-custody samples are available on the department's intranet site http://fyi.health.state.mn.us/phl/environmental/handbook/intranet/custodyprocedures.pdf

G. Sample Tracking

All samples that are analyzed in the laboratory follow a standardized tracking process. A "sample analysis request form" accompanies each sample when it arrives at the laboratory. The collector enters information about the sample on this form. A one-page set of instructions about completing the "sample analysis request forms" is provided to the collectors in the "MDH Environmental Laboratory Handbook". The handbook also covers information about ordering bottles, scheduling samples with the lab, delivering samples, and special custody guidelines. The handbook is posted at both the internal website: http://fyi.health.state.mn.us/phl/environmental/index.html and the external website: http://www.health.state.mn.us/divs/phl/environmental/handbook/internet/envhandbook.html

Information on all samples is entered into the laboratory's computer data base. First, the sample receiving staff records a unique laboratory sample number, which is then associated with all the analyses that are requested on the sample. The sample receiving staff also enters a project code ID and the received date. Labels which indicate which analyses are to be performed on each of the sample containers are then printed and put on the bottles. Secondly, the sample receiving staff enters information about the site, location, and the date and time of collection.

Samples are delivered from the sample receiving area to the Inorganic Chemistry Unit or the Organic Chemistry Unit to perform tests. All samples are stored separately from standards and reagents to prevent cross-contamination and are returned to the appropriate storage area after sufficient sample has been obtained for analysis. Sample fractions, extracts, and other items created during sample preparation are stored in accordance with the requirements of the analytical procedure.

Analysts use queries to generate work lists for analyses as needed. The printed sample numbers from the labels are used to identify their sub samples. A variety of queries to track progress and to generate workload summaries are used by the analysts, supervisors and management team.

H. Subcontracting of Analytical Services

When the laboratory is requested to analyze samples for tests it is not able to perform (either because the technology is not available or the capacity is not sufficient), the samples may be subcontracted to another laboratory. Subcontracting processes depend on the dollar amount of the work to be performed. If the project is >$25,000 and is performed over an extended period of time, then the laboratory must issue a formal Request for Proposals through the Minnesota Department of Administration and receive bids from other laboratories interested in performing the work.

For projects <$25, 000, the laboratory may choose from a qualified list of laboratories capable of performing the tests. For Safe Drinking Water Act compliance, a laboratory is chosen based on its certification status and approval through the state. For tests not certified by the state, the laboratory may choose a subcontractor that is certified through another agency appropriate to the testing requested. For example, the laboratory considers certification by the American Industrial Hygiene Association (AIHA) for analysis of metals in air samples.

The Operations Unit supervisor acts as the project manager and provides oversight to ensure that clients' needs are met. All subcontracted data are entered into the LIMS, and the subcontracted data report generated by the subcontracting laboratory is attached to the MDH final laboratory report.

I. Sample Storage

Samples are stored in walk-in coolers, refrigerators, shelving areas or temporarily on carts in the laboratory analytical areas. Storage conditions comply with the preservation and holding time requirements specified in regulation or method. More information on monitoring storage conditions is in Section 11.0 of this manual.

J. Sample Disposal

For routine (non-custody) samples, analysts in the Inorganic Chemistry Unit and the Organic Chemistry Unit monitor the received dates printed on the sample bottle labels. Personnel authorized by the unit supervisor dispose of most samples between 30 and 60 days after receipt. Water microbiology samples are discarded on the day of analysis. Personnel in the Sample Receiving Unit dispose of samples when final reports have been issued and storage space is needed for incoming samples.

The laboratory staff queries the LIMS for samples to be disposed. Custody samples are retained for at least 90 days after the report issue date or a date specified by the client during the project set-up. For custody samples, the Operations Unit will notify the client prior to disposal. The laboratory staff scans the sample barcode to record which sample containers the staff included in the disposal batch. The LIMS records the disposal and the date of the disposal for each scanned container.

All aqueous samples that are non-hazardous are neutralized (if needed) and enter the laboratory's general waste stream. The building contains a neutralization flow-through system in the basement area to filter and neutralize laboratory waste prior to entering the City of St. Paul sewer. The neutralization tanks are monitored at least annually for volatile and semivolatile organics, radiation, metals (including mercury), and pH. The laboratory

monitors the tank contents to determine point-source pollution and to take corrective action to avoid disposing of waste above regulatory limits. All soil/sludge samples that are non-hazardous are discarded as trash. Any hazardous samples are disposed according to the guidelines in the PHLD Chemical Hygiene Plan and the PHLD Hazardous Waste Manual. Both of these documents are accessible on the safety page of the PHLD website http://fyi.health.state.mn.us/phl/safety/index.html.

K. Records Retention

Paper copies of raw data, sample receipt documentation, quality assurance documents, and final reports are maintained at the laboratory for a minimum of one year and then stored at a records storage facility for a total of ten years from the date of creation. The lead/copper data germane to the Safe Drinking Water Act are retained for a total of twelve years from the date of creation. OSHA reports are kept as required by its program. Civil or criminal chain-of-custody documentation is retained at the laboratory for twelve years from the date of creation. Electronic copies of laboratory reports are maintained at the agency. Electronic records are backed up nightly by the information technology staff of MDH or the Office of Enterprise Technology, the statewide IT personnel, as appropriate.

SECTION 9.0: DATA QUALITY OBJECTIVES

Monthly, the laboratory management team (including the Quality Assurance Officer) meets with clients in the MDH Environmental Health Division and the Minnesota Pollution Control Agency to ensure compliance with the particular data quality objectives pertinent to the projects. Report limits for each field of testing are in the Environmental Laboratory Handbook (http://fyi.health.state.mn.us/phl/environmental/index.html). At the request of clients, report limits may be modified to meet data quality objectives of specific projects.

The laboratory works closely with its clients to develop Quality Assurance Project Plans (QAPPs) for specific studies. These QAPPs define the general problems that are being addressed as well as outlining the boundaries of the investigations, including the quality assurance activities conducted by the laboratory to ensure that the needs of the study are met.

SECTION 10.0: ANALYTICAL PROCEDURES

The laboratory analyzes samples from a wide range of matrices: drinking water, ground water, surface water, air, soils, sediments, tissue, and wastes. The Laboratory's internal Standard Operating Procedures (SOPs) are based on reference methods developed or approved by various state and federal agencies. The analytical procedures and reference methods used by the Environmental Laboratory Section for various state and federal programs are listed in the Environmental Laboratory Handbook. The handbook does not list sensitive information, such as the procedures and methods for chemical terrorism response.

The handbook is posted at both the internal website: http://fyi.health.state.mn.us/phl/environmental/index.html and the external website: http://www.health.state.mn.us/divs/phl/environmental/handbook/internet/envhandbook.html

The actual analytical procedures used by the laboratory are described in its Standard Operating Procedures (SOPs). Copies of the analytical procedures are on file in the laboratory's Quality Assurance Office and in the pertinent units of the laboratory. The internal website http://fyi.health.state.mn.us/phl/environmental/index.html is used for controlled copy distribution to all staff. The reference methods are on file with the laboratory's Quality Assurance Officer.

SECTION 11.0: EQUIPMENT AND SUPPLIES

A. Maintenance

A current equipment inventory is maintained; the inventory is updated as needed and includes itemization of spare parts stored at the laboratory. Except where available online, the laboratory ensures that copies of instrument manuals are accessible to the analyst either by storing near the instrument or on a bookshelf in the laboratory area.

Before being placed into service, laboratory equipment is calibrated or checked to establish that it meets the required specifications to produce quality data.

Laboratory equipment is maintained according to the manufacturer's specifications and in such a way that the quality control requirements of the laboratory are met for all analyses performed. The laboratory maintains a record in the LIMS of all regularly scheduled preventive maintenance for the equipment. In general, the laboratory maintains a preventive maintenance contract with Specialty Underwriters for major analytical equipment (e.g. the mass spectrometry instruments, the ion chromatography, the alpha-beta radiation chemistry instruments, and others). The contract is managed by the State of Minnesota Department of Administration and reviewed internally by the individual testing unit supervisor. Other instrumentation is maintained and repaired by the unit supervisor or experienced analyst. Appendix 7, pp. 49-50, contains examples of equipment maintenance logs to show representative items recorded in the LIMS.

B. Monitoring Conditions

Where required or needed for internal quality control, temperatures for walk-in coolers, refrigerators, ovens and water baths are electronically monitored and logged using an Isensix™ system. The system operates through a series of remote radio-controlled sensors with uniquely identified thermocouples at each monitoring location. Acceptance ranges for each monitored area are programmed into the system to activate various alarm categories ranging from an audible alarm to a phoned alert message sent to an individual or group of individuals responsible for monitoring the storage or analytical conditions. When alarms are

silenced (either locally or remotely), the system requires documentation of the user identification and a comment. This information is stored in the Isensix™ database along with the system's automatic log of the resulting action. Pre-programmed actions are in place to allow the system to auto-correct when warming or cooling is required. Data can be retrieved from the database either in tabular or graphic form. Thermocouples are calibrated on-site by an Isensix, Inc. technician once a year.

In instances where monitoring or control is specified in a test method or by regulation, the laboratory shall meet and document adherence to those monitoring requirements.

C. Procurement of Supplies

Procedures for the procurement of chemicals and supplies and information on safety and proper handling of chemicals are documented in the Public Health Laboratory Division (PHLD) "Chemical Hygiene Plan" as posted on the division's intranet site http://fyi.health.state.mn.us/phl/safety/chemhygieneplan.pdf.

For high-turnover, consumable, laboratory supplies, the purchasing system automatically re-stocks the item at a pre-set interval or to maintain stock levels. For specialty items, such as gas chromatography columns, the unit supervisors or their designees submit requests to purchasing personnel as needed. Each unit monitors its own stock of supplies and orders more when needed. Shared gases which are piped through the laboratory from the loading dock area have re-stocking procedures pre-arranged with the vendor. The laboratory has the ability to request emergency purchases which can be delivered overnight.

Specialty gases are categorized as bulk gases (piped from the loading dock area through the building), manifold gases (piped from the gas-manifold storerooms through the building), and point-of-use gases. Argon and nitrogen are supplied as bulk gases. The argon tanks are assembled into a primary and a backup bank of tanks. When the primary tanks are emptied, the manifold automatically switches to the backup tanks. New argon tanks are delivered every two weeks or as needed. The liquid nitrogen supply is monitored remotely by the vendor. When the tank level falls below a pre-set mark, the vendor is automatically notified via phone that re-stocking is needed.

The gas-manifold room has both a primary and a backup bank of helium gas cylinders. When the primary tanks are emptied, the manifold automatically switches to the backup tanks, and a light indicates that the backup tanks are in use. The laboratory routinely monitors the gas usage rate and takes corrective action if any possible "overuse" could be attributed to a leak in the system. The normal turnover rate is 1-1 ½ weeks per bank.

For selected specialty gases, the cylinders are kept at the instruments and monitored regularly by the analysts. For radiation chemistry, the liquid nitrogen used in the gamma instruments is monitored by the analysts and refilled weekly.

SECTION 12.0: CALIBRATION

A. Analytical Balances
Laboratory staff members maintain the analytical balances. Staff checks the calibration daily by analyzing weights that are near the approximate weight of material that will be determined. An external vendor calibrates the analytical balances annually to NIST-traceable standards. The Quality Assurance Officer is responsible for contracting a qualified vendor to calibrate the analytical balances to specified ranges determined by individual manufacturers. The QA Officer also is responsible for tracking, verifying calibration results, and maintaining accurate records of calibration data sheets.

B. Weight Sets
The weight sets for each analytical unit are calibrated every five years by an external vendor. The vendor is responsible for calibrating the weight sets and supplying MDH with a Certificate of Calibration. The Quality Assurance Officer is responsible for tracking, sending out, verifying weights are returned within acceptable limits, and maintaining accurate records of Certification of Calibration certificates for each weight.

C. Mechanical Pipettes
The mechanical pipettes are calibrated semi-annually by an external vendor to ensure accurate and precise delivery of measured volumes of standards. The Quality Assurance Officer is responsible for contracting a qualified vendor to calibrate pipettes to specified ranges determined by individual manufacturers. The QA Officer also is responsible for tracking, verifying calibration results, and maintaining accurate records of determined calibrations.

D. Analytical Instruments
Calibration procedures for analytical instruments are specified in the laboratory's standard operating procedures. At a minimum, the calibration procedures meet the requirements of the approved method.

SECTION 13.0: QUALITY CONTROL

A. QC in the QA Manual and in SOPs
The QC policies and procedures listed herein are standardized for use in this laboratory. Employees in this laboratory recognize that, in some cases, a particular USEPA-approved method and, in turn, a particular Standard Operating Procedure (SOP) may describe different QC policies and procedures. In those situations, the QC policies and procedures in the SOP supersede those in this Quality Assurance Manual.

B. Detection Level

The policy and procedure for conducting a Detection Level Study are described in Appendix 8, pp. 51-52. The worksheet for determining the Method Detection Limit (MDL) for analyses involving single analytes is provided in Appendix 9, p. 53. Instructions for completing this worksheet are provided in Appendix 9, pp. 54-56.

C. Initial Demonstration of Capability
The policy and procedure for conducting an Initial Demonstration of Capability Study are described in Appendix 10, pp. 57-58.

D. Report Level Verification
The policy and procedure for conducting a Report Level Verification are described in Appendix 11, pp. 59-60.

E. Other QC Checks
The analytical Standard Operating Procedures (SOPs) for each field of testing list the quality control procedures that are required for laboratory staff. At a minimum, the SOPs include the following:

For chemistry and radiochemistry, the quality control included or referenced:
- instrument performance check standards;
- frequency and acceptability of method detection limit (MDL) calculations;
- frequency and acceptability of demonstration of low-level capability;
- calibration, internal and surrogate standards;
- laboratory reagent blank, field reagent blank and trip blank;
- field and laboratory matrix replicates;
- quality control and proficiency testing samples;
- laboratory control sample and matrix spike replicates;
- initial demonstration of method capability;
- use of control charts;
- qualitative identification/confirmation of contaminants.

For microbiology the quality control included or referenced:
- positive and negative culture controls;
- confirmation/verification of presumptive total-coliform-positive samples;
- sterility controls;
- proficiency testing and quality control samples.

SECTION 14.0: DATA REDUCTION, VERIFICATION, VALIDATION, AND REPORTING

The laboratory performs data reduction and validation in accordance with the requirements in the approved methods and as cited in the Code of Federal Regulations. The laboratory uses

the USEPA guidance documents (as cited in Section 16.0) and clients' project-specific quality assurance plans to validate the data produced.

A. Reduction and Validation Process

Raw data are transformed into reportable results using mathematical calculations and analyte identification obtained from direct readings from instruments or calculations based on instrument output, readings or response. Data reduction activities may be conducted manually by analysts converting analytical output to sample concentrations using calculations, or automatically, using instrument or other validated computer software. The laboratory maintains records demonstrating that the calculations provide the expected results. Factors such as dilution, sample weight, sample volume, and significant figures are accounted for in data reduction formulas described in each standard operating procedure.

Manual integration is allowed if peaks are not properly integrated by the instrument software. All manually integrated peaks are clearly identified and documented to show how and why the manual integration was selected over the automated peak integration result.

Analytical batches include QC data as specified per the method requirements and client requests. When the analyst batches samples, the LIMS will add appropriate QC samples to the run log to assure the analysis includes method-required QC and client-requested QC items. The LIMS captures results of QC sample analysis from the instrument and allows the laboratory staff to plot control charts from QC data. Typically, the laboratory staff monitors results of matrix spike, matrix spike duplicates, sample duplicates, laboratory control samples, blanks, and various other measurements. For QC plotting, the laboratory staff may select the number of points to include in a graph or viewable data. In some cases, additional data are needed for monitoring trends, and the analysts may query additional data or display a larger number of points from the analysis dates selected.

Method-required limits or in-house acceptance limits are set for each method and matrix analyzed. Acceptance limits may also be specified by the client to meet a data quality objective (DQO). If QC results are within acceptance limits, the LIMS will allow reporting of the results without further qualification by the analyst. When sample results do not meet the acceptance limits, the LIMS highlights the affected results and requires acknowledgment or further action from the analyst before the sample results may be reported. Acknowledgment may include re-analysis of the samples or, if the analysis cannot be repeated, the results may be flagged with a data qualifier(s) indicating which acceptance limits were not met.

The laboratory may issue results either electronically or via printed copy, depending on the need of the client. When the analyses for all samples on one work order are completed, the LIMS generates a final report and puts it into a review queue. The unit supervisor or designated analytical staff receives a notice that data are ready for review. The electronic

copy of the data is reviewed and approved in the LIMS. The review process is used to assure that the sample results are reported without systematic errors, that samples are analyzed within holding times, that instruments are within calibration, and that the QC data are within the acceptance limits or flagged accordingly. A discrepancy found during the review process triggers a recheck of data or reanalysis of the samples. Once the unit supervisor or designated analytical staff approves the data, the LIMS recognizes the approval as an authorization to release the final report.

B. Reporting

At times, the client may need to view data prior to the final review and approval. Any authorized user can generate a preliminary report. All preliminary reports are indicated as such in the header of the report. Some clients are also authorized by the laboratory to view reports via a secure, password-protected, internet-based application.

Reports that have been amended are indicated as such in the header of the report. In addition, the item(s) in the report that have been changed are described at the end of the report with the corrected value reported alongside the previous value.

SECTION 15.0: SYSTEM AUDITS

A. Proficiency Testing

The laboratory participates in proficiency testing (PT) studies for the SDWA, CWA, RCRA, and OSHA programs to demonstrate laboratory capability for analytes of interest. The samples are purchased from approved providers certified by the American Association for Laboratory Accreditation (A2LA, a NELAP-recognized proficiency testing oversight body) that require analytical quantification within the acceptance limits established by USEPA and the NELAC standard. The true value of the concentration of the reference material is unknown to the laboratory at the time of the analysis. The PT samples are managed, analyzed, and reported in the same manner as routine samples.

Additional measures to demonstrate proficiency may be required for individual projects. The scope and requirements of the proficiency program are generally presented to the laboratory in specific quality assurance project plans (QAPPs).

Proficiency testing results are reviewed by the Laboratory Quality Assurance Officer and the reports are distributed to the Laboratory Supervisors. The unit supervisors are responsible for distributing the individual results to each staff member who participated in the PT studies.

Acceptable performance on PT samples is required to establish and demonstrate ongoing capability for the various analytical systems, methods, and matrices. In the event of

unacceptable proficiency testing results, the federal or state regulatory agency is notified within 30 days of corrective action, including documentation stating the purchase of a remedial PT sample. Additionally, the laboratory authorizes the approved PT vendor to electronically supply results directly to the regulatory agency.

B. Internal Audits

The Quality Assurance Officer, or qualified designee, performs internal audits of the laboratory areas at least once per year to verify that the guidance provided in this document and other related documents are being followed. Internal audits may be performed at any time to investigate any result or procedure that is out of specification. To qualify as a designee to the Quality Assurance Officer for the purpose of conducting an internal audit, personnel must be independent of the activity being audited and must demonstrate knowledge of the tasks to be reviewed.

When performing an audit, the Quality Assurance Officer or qualified designee examines the following areas: recordkeeping, sample handling, reporting and archiving, quality and tracking of standards and reagents, appropriate use of sample containers, glassware preparation and storage, generation and use of control charts, and completeness of training records. Inspections of other areas or documents may be necessary to evaluate the root cause of a deviation from procedures. The Quality Assurance Officer, or qualified designee, reviews the SOP prior to the audit to assure written protocols are being followed. Checklists for conducting the audit are developed by the Quality Assurance Officer or are obtained from an external source (i.e. other states and The NELAC Institute's quality system checklist). Previous audit findings are reviewed prior to an internal audit to assure that corrective actions have been implemented.

After completing an internal audit, the Quality Assurance Officer supplies a copy of the completed checklists, which serves as the report to laboratory management and unit supervisors of any deviations from approved procedures or policies. The unit supervisor or designated laboratory staff members prepare a response and corrective action plan which includes any recommendations to management that might assist in improving the quality of the data being generated. If the proposed actions are acceptable, the Quality Assurance Officer files a copy of the report, the laboratory's response, and any follow-up documentation indicated in the corrective action plan. Follow-up audit activities are employed to verify and document the implementation of the corrective action plan. The complete audit record is available for review by the USEPA Region 5 certification officer.

C. External Audits

External laboratory audits can determine adherence to established and documented sample collecting, handling and documentation procedures. Audits are performed at the discretion of

the Certification Officer from the USEPA Region 5 Office of Water. Results of the audits are reported by the USEPA to the laboratory, identifying any areas in which corrective action is needed. After correction of any deficiencies, the laboratory will respond to the USEPA to document the corrective actions taken.

Certification for analyses in drinking water is issued by the USEPA Region 5 Office of Water. A copy of the current drinking water certification is included in Appendix 12, pp. 61-64. The document is entitled "Enclosure A: Laboratory Certification Summary, Minnesota Department of Health (May 5-7, 2008).

D. Corrective Action Policy

A corrective action form is required when departures from the established quality assurance and quality control policies and procedures occur or in the event of a proficiency test (PT) failure. (Appendix 13, pp. 65-66, contains a corrective action form for use with a non-conformance of work or a failed PT sample.) All non-conformance activities and PT failures require an investigation and documentation of potential causes and corrective actions. Corrective actions are initiated when the Quality Assurance Officer assigns a corrective action form to an occurrence of non-conforming work after notification of the event by an analyst or Supervisor. The Quality Assurance Officer may assign an investigator who is independent of the analyst or Unit Supervisor. The laboratory analyst or designated investigator completes and signs the Corrective Action Form, submits it to the Unit Supervisor for review and signature, and returns it to the Quality Assurance Officer within two weeks. The completed Corrective Action Form and copies of all documentation of corrective actions are maintained by the Quality Assurance Officer. Upon completion, a copy of the Corrective Action Form is forwarded to the Environmental Laboratory Section Manager for review. The Quality Assurance Officer reviews the proposed plan and verifies the corrective action progress and effectiveness.

Problems arising during or after analysis of samples may also require corrective actions; however, the investigation of such problems is carried out by the analyst generating the data or by the designated reviewer or Unit Supervisor reviewing the data. Corrective actions are described in standard operating procedures for the test methods used in the laboratory. If an analyst determines that corrective actions have not resolved the problem or that a data set is compromised, the analyst must notify their Supervisor immediately. The Unit Supervisor must assess the data and determine if, and how, the data may be qualified. This process may require contact with the client and written instructions on how to proceed. The Unit Supervisor may conclude that the effectiveness of the corrective actions should be investigated further and requests a corrective action form from the Quality Assurance Officer.

SECTION 16.0: REFERENCES

"Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, Revised March, 1983.

"Methods for the Determination of Metals in Environmental Samples," EPA/600/4-91/010, June, 1991.

"Standard Methods for the Examination of Water and Wastewater," 20th Edition, APHA, AWWA, WPCF, Washington, D.C. (1998).

"Methods for the Determination of Organic Compounds in Drinking Water," EPA/600/4-88/039, Revised July, 1991.

"Methods for the Determination of Organic Compounds in Drinking Water," Supplement 1, EPA 600/4-90/020, July, 1990.

"Methods for the Determination of Organic Compounds in Drinking Water," Supplement 2, EPA/600/R-92/129, August, 1992.

"Prescribed Methods for Measurement of Radioactivity in Drinking Water," EPA 600/4-80-032.

"EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations," EPA QA/R-5, Draft, January 29, 1993.

"Manual for the Certification of Laboratories Analyzing Drinking Water", 5th Edition, USEPA, January, 2005.

"Microbiological Methods for Monitoring the Environment," EPA/600/8-78/017, December, 1978.

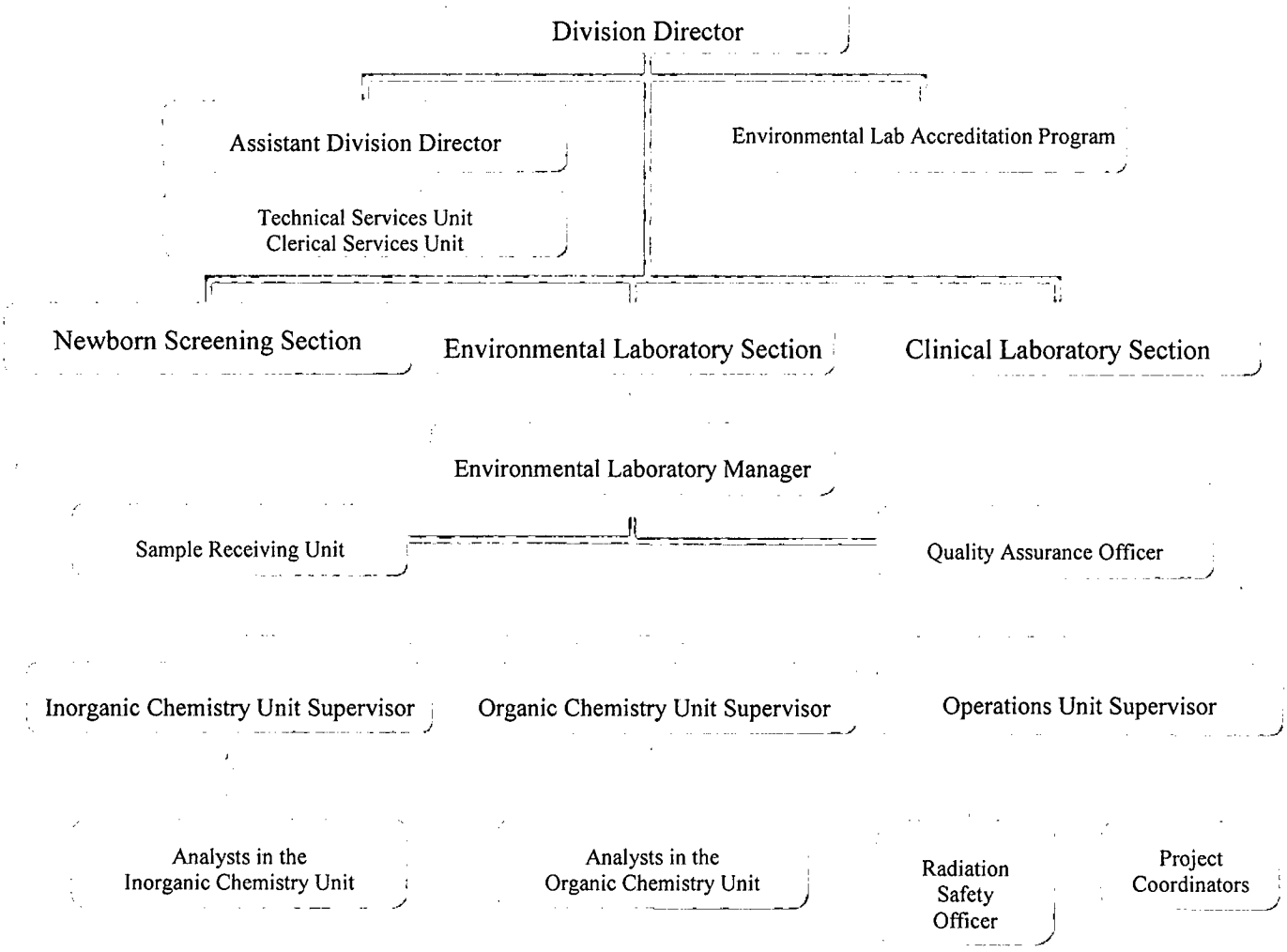
Minnesota Department of Health Environmental Laboratory Sample Receiving Procedure Manual, Rev. 4, Laboratory Information Management Systems and Technical Services Section (2006).

"IUPAC. Compendium of Chemical Terminology, 2nd ed." (the "Gold Book"). Compiled by A. D. McNaught and A.Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook. Last update: 2009-02-17; version: 2.0.3.

SECTION 17.0: APPENDICES

The Table of Contents for the Appendices is presented on p. 5 of this Quality Assurance Manual. The appendices are on pp. 38-63.

Appendix 1
PHLD organizational chart, focusing on the environmental testing units



Appendix 2
Training Record for an Individual Standard Operating Procedure

MDH Environmental Laboratory

Document Number: 2006-02

ANALYST: _____ ANALYSIS / AN CODE: _____

		Date Completed	Trainer	Trainee	Comments
Received MDH SOP					
Read MDH SOP					
Read Reference Method					
Reviewed Methods with Trainer					
Reviewed Waste Management Procedures with Trainer					
Watched Method Performed					
Performed Method (supervised)	Date #1				
	Date #2				
	Date #3				
Completed MDL Study					
Completed IDC Study					

Additional Comments and Notes:

I (we) certify that the training for this method has been completed.

I agree to follow this method as presented. I agree that I will not make changes to this method without supervisor's approval.

_____
trainer 1 signature / date

_____
trainer 2 signature / date

_____
analyst signature (at completion of training) / date

Appendix 3
Record of Personnel Education and Training

MDH Environmental Laboratory
Quarterly Period (Select One):
Jan-Mar 2006
Apr-Jun 2006
Jul-Sep 2006
Oct-Dec 2006

Document Number : 2006-01 .

Record of Personnel Education and Training

Please Print

Employee Name: _____
Job Title: _____

Instructions are on the back of this sheet.

Date	Type of Instruction	Training Activity	Trainer's Name	Hours

Trainee's Signature: _____ Date: _____
Supervisor's Signature: _____ Date: _____

Appendix 4
Sample analysis request form (a.k.a. Chain of Custody form): Example of a form used by MDH Environmental Health Division

1	2	3	4

Minnesota Department of Health
Section of Drinking Water Protection
Environmental Laboratory Request Form

Program Code	ID Number	Facility Name	City, Town, Township	
Date Collected (for all samples on form)	Collector ID	Collector Name	Original Sample Number	Comm. Sanitary Survey Date
Sample Type	Your Chlorine Residual Result mg/l	Sampler Comments		

	Field Number	Location ID	Sampling Point	Time Collected am☐ pm☐	Temp
1					
2					
3					
4					

Lab Comments

BACTICHEM		1	2	3	4
Total Dissolved Solids	5				
pH	13				
Conductance	14				
Alkalinity	22				
Chloride	23				
Sulfate	293				
Silica	30				
Fluoride	29				
Total Phosphorous	59				
Ammonia-N	64				
Nitrite-N	67				
Nitrate+Nitrite-N	69				
Cyanide, Free	26				
TOC	98				
DOC	99				
MF-Total Coliform	308				
PA-Total Coliform	327				
PA Total Coliform QT	338				
UV254	54				
SUVA	56				
Lab Use Only					

METALS		1	2	3	4
Antimony	635				
Arsenic	110				
Barium	117				
Beryllium	640				
Cadmium	134				
Chromium	131				
Copper	147				
Iron	156				
Lead	160				
Manganese	170				
Mercury	637				
Nickel	175				
Selenium	180				
Thallium	238				
Ca as CaCO3	208				
Mg as CaCO3	209				
Potassium	644				
Sodium	645				
Hardness	239				
IOC (Excl. methods 26, 637)	753				
Bromate	295				
Chlorite	295				
Chloride/Bromide	296				

ORGANIC		1	2	3	4
BNAs by GCMS	407				
Carbamates	408				
Glyphosate	409				
Herbicides	415				
Gas/Fuel	463				
VOC - THM	464				
VOC – Full List	468				
PAH Group	470				
Haloacetic Acids	411				
PFC Expanded	555				
UCMR	527				
UCMR	529				
RADIATION					
Radium-226, -228	807				
Gross Alpha	816				
Uranium	798				
Radon, Water	809				
ANALYSIS GROUP					
General Chemistry Group	*10*				
Nitrogen Group	*19*				

Rev. 11/07/2008

http://fyi.health.state.mn.us/phl/environmental/index.html

Sample analysis request form (a.k.a. Chain of Custody form): Example of a form used by the Minnesota Pollution Control Agency

A	B	C	D	E

Minnesota Pollution Control Agency

MDH Stream / Lake Lab Sheet

Collected by:_____ Project Code: ___ ___ Date/Time Rec'd by Lab: _____

MDH ID:_____ Report to: _____ Phone: _____

Signature on Chain of Custody block is mandatory. See back of this page.

SAMPLE INFORMATION	A	B	C	D	E
STORET PROJECT ID*					
STORET STATION ID					
FIELD ID (Project Station ID) / LAKE NAME					
DATE (MM/DD/YY)					
TIME (Military)					
SAMPLE DEPTH (TOP) m (Lake Only)					
SAMPLE DEPTH (BOT) m (Lake Only)					
SITE ID (Lake Only)					
ANALYSIS GROUP NO.**					
Quality Assurance***					
FILTER VOLUME (for chlorophyll a)					
LAB TEMP (°C)					

* Identify Project ID for sample collection (examples: LAKETREND, LAKE_LAP)
** See Back to Select an Analysis Group Identified by a Number Code
*** FD = Field Duplicate/Replicate, SB = Sampler Blank, SS = Split Sample, TB = Trip Blank, BB = Bottle Blank, EB = Reagent Blank
ENTER THE ORIGINAL AND QA SAMPLES IN SEPARATE COLUMNS

Write the TOTAL NUMBER of each bottle type collected at the top of each associated column below.

BACTICHEM (Hold Time) Plastic General Bottle	MDH #	A	B	C	D	E
Alkalinity, Total (14 d)	022					
BOD, 5Day- *2L bottle* - (48 hr)	096					
CBOD, 5Day-*2L Bottle*-(48 hr)	083					
Chloride, Total (28 d)	297					
Color (48 hr)	012					
Chlorophyll-*a*, Lab Filter (48hr)	452					
Conductivity (28 d)	014					
Nitrite, Nitrogen Total (48 hr)	067					
pH Lab (Immediate)	013					
Phos-Total Ortho (48 hr)	063					
Solids, Susp. Volatile (7 d)	004					
Solids, Total Dissolved (7 d)	005					
Solids, Total Susp. (7 d)	003					
Solids, Total Volatile (7 d)	002					
Solids, Total (7 d)	001					
Sulfate, SO_4 Total (28 d)	293					
Turbidity (48 hr)	011					
Lab Filter (48 hr)	010					
Lab Use only.						

BACTICHEM (Hold Time) Plastic Sulfuric Acid Bottle	MDH #	A	B	C	D	E
Carbon, Dissolved Org (28 d)	099					
Carbon, Total Org (28 d)	098					
COD, Total (28 d)	097					
Ammonia Nitrogen, Total (28 d)	064					
N-Org, Total (28 d)	065					
Kjeldahl Nitrogen, Total (28 d)	068					
NO_2+NO_3-N, Total (28 d)	069					
Phosphorus, Total (28 d)	059					
BACTICHEM (Hold Time) Plastic Sterile Bottle	**MDH #**	**A**	**B**	**C**	**D**	**E**
E. coli-MPN (24 hr)	335					
METALS (Hold Time) Plastic Nitric Acid Bottle	**MDH #**	**A**	**B**	**C**	**D**	**E**
Calcium, $CaCO_3$ (180 d)	251					
Iron, Total (180 d)	152					
Potassium, Total (180 d)	255					
Sodium, Total (180 d)	257					
BACTICHEM (Hold Time) Glass Fiber Filter	**MDH #**	**A**	**B**	**C**	**D**	**E**
Chlorophyll-*a*, Field Filter (7 d)	450					
Pheophytin-*a* (7 d)	451					

MDH Copy ⇓ See Back for Analysis Groups, Project Codes and Chain of Custody ⇓ mlk revised 04/09

Appendix 5
Chain of Custody form for receipt of samples including those subject to criminal or civil custody

MINNESOTA MDH DEPARTMENT OF HEALTH

Chain of Custody

Minnesota Department of Health
Environmental Laboratory
601 Robert St. North
St. Paul, MN 55155-2531

Page ____ of ____

Lab Use Only.

Potential Hazard: Yes/No/Unknown (Circle One).
If Yes please add information to Comments below.

Standard/Civil/Criminal Chain of Custody
(Circle One)

Client/Agency_____
Project Name_____
Site ID_____
Program Code (2 Letters) ___ ___
Contact Name_____
Contact Phone #_____

Matrix Codes:
DW = Drinking Water
SW = Surface Water
GW = Ground Water
WW = Waste Water
SD = Soil/Solid
WP = Wipe
AR = Air
TS = Tissue
OT = Other

Report to_____
MDH ID_____
_____
_____
_____
Address If Needed

Sampled By (Print) Affiliation
Sampler Signature Phone

Containers & Preservatives

#	MDH Sample Number (Lab Use Only)	Field ID	Sample Source/Point	Collection Date	Time (24 Hour)	Matrix Code	Unpreserved	Hydrochloric Acid	Sulfuric Acid	Nitric Acid	Sodium Hydroxide	Sodium Thiosulfate	Ascorbic Acid	Other	Total # of Containers	Sample Field Filtered Y/N	Requested Analysis:	Sediment Y/N	Lab Temp (C)
1																			
2																			
3																			
4																			
5																			
6																			
7																			
8																			
9																			
10																			

Sampler Comments:

Receiving Comments:

Relinquished By / Affiliation	Date	Time	Accepted By / Affiliation	Date	Time
(Sampler)					

White Client Copy Yellow Lab Copy Pink Submitter Copy

MDH 1000

Appendix 6
Chain of Custody logbook page
to internally track enforcement samples

000250

MDH-CHEMICAL LABORATORIES
CHAIN OF CUSTODY LOG

Sample Number(s): _____ Bottles Rec'd. Sample Number(s)
Chain of Custory Record #: _____
Site: _____
Matrix: _____
Sampler: _____
Accepted By: _____/_____/_____
Name /Date /Time
Numbered By: _____/_____/_____
Name /Date /Time

CUSTODY TRANSFER RECORD

SAMPLE NUMBER(s)	BOTTLE TYPE	CHECKED OUT				CHECKED IN			
				INITIALS				INITIALS	
		DATE	TIME	ANALYST	C OF C OFFICER	DATE	TIME	ANALYST	C OF C OFFICER

COMMENTS_____

(HE-01287-02) (3/87)

Appendix 7
Equipment maintenance: example
Daily maintenance of an ICP-MS instrument

Perkin-Elmer Elan DRC II Daily Maintenance

Serial Number: Z0130310 Month: May Year: 2009

Date	1(F)	2(S)	3(S)	4(M)	5(T)	6(W)	7(T)	8(F)	9(S)	10(S)	11(M)	12(T)	13(W)	14(T)	15(F)
HARDWARE Checklist															
Ar Tank Pressure (psi)															
Reaction Gas Type/Pressure (psi) Cell gas A															
Reaction Gas Type/Pressure(psi) Cell gas B															
Chiller Pressure(psi)/Temp (°C)															
Torch Box Temperature (°C)															
Inspect Cones (if necessary)															
Inspect Sample Introduction System															
DAILY PERFORMANCE CHECK															
Running vacuum pressure (10^{-6} T)															
Neb Flow (L/min., Std mode)															
RF Power (kV)															
Lens voltage (V)															
Autolens															
^{24}Mg Sensitivity (cps, Std Mode)															
^{115}In Sensitivity (cps, Std Mode)															
^{238}U Sensitivity (cps, Std Mode)															
^{84}Kr Sensitivity (cps, Std mode)															
^{208}Pb Sensitivity (cps, Std mode)															
$^{156}CeO/^{140}Ce$ (%)															
Ba^{++}/Ba (%)															
Background (cps, 8.5 /220 amu)															
ANALYST															

If daily performance results are not acceptable, perform instrument optimization. See optimization Worksheet.

Equipment maintenance: example
Monthly repairing and maintenance of an ICP-MS instrument

Perkin-Elmer Elan DRC II Monthly Repairing and Maintenance Log

Serial Number: **Z0130310** page 1

DATE	WHO	PROBLEM & SOLUTIONS

Appendix 8

Policy and Procedure for Detection Level Study

for the Environmental Testing Units of the Public Health Laboratory Division, Minnesota Department of Health

A Detection Level (DL) Study must be performed for each method, for each environmental matrix, for each analyte, and for each instrument as part of an Initial Demonstration of Capability (IDC) and periodically thereafter as described below. This requirement pertains to inorganic and organic chemical analyses; it is not applicable to microbiological and radiological analyses. The Quality Assurance Officer (QAO) may waive this requirement when it is not feasible to conduct a DL study.

The analyst must follow requirements for the performance of a DL study cited in the reference method or applicable regulatory program for which the data are to be used. A project or client may also specify the type of Detection Level Study. If no such requirements exist, the analyst shall utilize the DL procedure described in #1 below. The analyst, with the approval of the QAO and the Supervisor may choose the procedure outlined in #2 below as an alternative to an MDL when they have determined that it is more appropriate.

1) Method Detection Limit (MDL): The study must be performed as described in Appendix B to Part 136 – Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11. The calculated MDL must meet the acceptance criteria established for each analysis or analyte by the Quality Assurance Officer.

2) Minimum Reporting Level Confirmation (MRLC): The MRLC is described in the UCMR2 (Unregulated Contaminant Monitoring Regulation) Laboratory Approval Manual, version 2.0, October, 2006. For the MRLC, fortify, extract, and analyze seven replicate laboratory fortified blanks (LFBs) at or below the MRL concentration. These LFBs must: contain all method preservatives described in the method, contain each analyte of interest at concentrations at or below the MRL, and be processed through the entire method procedure (ie. including extraction, where applicable). The mean and standard deviation are calculated. Using the formulas in Section 7 of the UCMR2 Laboratory Approval Manual, calculate HR (half range for the prediction interval of results), upper PIR (prediction interval of results) limit and lower PIR limit. The recoveries must meet the acceptance criteria established for each analysis by the Quality Assurance Officer. (Note: the UCMR2 requires that the upper PIR limit must be $\leq$ 150 % recovery and the lower PIR limit must be $\geq$ 50% recovery).

Frequency of Detection Level Studies: With regard to the frequency of Detection Level Studies, the laboratory must follow any requirements cited in the reference method or applicable regulatory program for which the data is to be used. If no such requirements exist, the frequency of a Detection Level Study is determined as follows:

1) Initially as part of an IDC for each combination of method, environmental matrix, and instrument.
2) At the discretion of the Unit Supervisor, as part of an IDC for each analyst performing the analysis. (Note: MN Rules do not require an MDL.)

3) Whenever significant changes affecting the sensitivity of the analysis occur in the SOP, matrix or instrument as determined by the Quality Assurance Officer (in consultation with the analyst and Unit supervisor).
4) When any other change occurs that, in the opinion of the Quality Assurance Officer, could significantly affect the precision or accuracy of the analysis.

Documentation and other requirements: The Detection Level Study option chosen, including the acceptance criteria, and corrective actions that the analyst must take if the acceptance criteria are not met, must be described in the SOP for both the IDC and any ongoing DL study. The frequency of any required ongoing DL must also be stated in the SOP. The Detection Level Study must include all of the steps in the analysis including sample preparation and processing. For purposes of this policy and procedure, an environmental matrix may include multiple matrices (example: drinking water and non-potable water may be grouped together), so long as each matrix is processed and analyzed in a similar manner as part of a single SOP. The written SOP must list all of the matrices for which it is applicable.

Note: The effective date of this document is the date of the last signature on this document. On the effective date, this document becomes an appendix to the *Quality Assurance Manual for the Environmental Testing Units of the Public Health Laboratory Division.*

Appendix 9
Method Detection Limit (MDL) Single Analyte Worksheet *and* MDL Worksheet Instructions

Minnesota Department of Health
Environmental Laboratory
Method Detection Limit (MDL) Single Analyte Worksheet

Target Analyte: _____
MDH LIMS Code: _____
Date submitted: _____

MDL Study: **1st** **2nd** **3rd**

Analyst:		Analytical Method:	
Matrix:		Prep Method:	
Instrument ID:		Reported Units:	

Replicate	An Date	Result	% Recovery
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			

MDL = Std.Dev. x Student's t

Report Level: _____
True Value (TV): _____
Number of Points: _____
Mean = _____

% Recovery = _____
Std. Dev. (n-1) = _____
Student's t: _____

MDL = _____

TV/MDL = _____

TV/MDL between 1 and 10?
Is MDL ≤ RL?
TV ≤ RL?

t7 =	3.143
t8 =	2.998
t9=	2.896
t10=	2.821
t11=	2.765
t12=	2.718

QAO Comments:

Approved by QAO: _____
Init. & date

MDL Study entered: _____
Init. & date

MDL Single Analyte Worksheet Instructions

prepared by Keith Peacock, 2-23-07

1. These instructions are applicable to the single analyte MDL worksheet. There are two forms of this worksheet: 1) a blank form that the analyst can generate and then fill in by hand and 2) a form that has all of the calculations built into the spreadsheet and designed to be completed electronically. These worksheets should not be used for multi-analyte analyses.

2. In the upper right hand corner of the MDL worksheet, enter the target analyte, MDH LIMS code and the date you are submitting the worksheet to the QA Office. Also indicate if this is the first, second or third study for the same analyte that is being submitted within a 3 month period.

3. For "analyst", use your LIMS name. Analytical method refers to the reference method for the applicable SOP. If the MDL standard you used was prepared like a sample (digested, extracted, etc.) describe that, otherwise enter N/A.

4. All values must be recorded in the same units.

5. It is recommended that a starting point for the MDL standard be either: 1) a standard prepared that is at or near the report level (RL) or 2) a standard at a concentration between 1 and 5 times the anticipated MDL.

6. A minimum of seven replicates is required. MDL data can be generated from a single analytical run. However, to generate the most variability, the data should be generated over a period of at least 3 days but no more than 2 months.

7. If target analytes are present in the reagent water used to prepare the MDL standards that can significantly affect the recovery of the analyte, seven blanks are analyzed and the average of the seven is calculated. This amount is then subtracted from the (found) results for each replicate. The MDL is then calculated from these adjusted concentrations. Prior approval from the supervisor and QA Officer is necessary.

8. All the results obtained from the replicates should be used in the MDL calculation, unless the analyst knows for certain that a result is not valid.

9. Enter the report level for the analyte and the True Value (TV) of the MDL standard that you used to generate the data.

10. Enter the results for each replicate; record raw numbers without rounding (attend to significant figures). Calculate the % recovery for each replicate.

11. Calculate the mean of the results of the MDL standard and the average % recovery. Percent recovery of the replicates should be reasonable for that analyte, but no universal criteria for percent recovery have been established.

12. Calculate the standard deviation for n-1 and enter that value.

13. Select the Student's t value corresponding to the number of replicates or n (done automatically if using the MDL calc spreadsheet).

14. Multiply the Student's t value x the Standard Deviation to get the MDL value.

15. Divide the True Value of your MDL Standard by the calculated MDL and enter that result.

16. Then answer the questions shown.

17. As a guideline, the following criteria should be met for an acceptable MDL study:

    1) The true value (TV) of the standard should be within the range of 1 to 10 times the calculated MDL. If the calculated MDL is greater than the TV of the standard (TV/MDL < 1), the MDL study should be repeated with a standard of higher concentration. If the TV is greater than 10 times the MDL (TV/MDL > 10), the MDL should be repeated with a standard of lower concentration, unless the TV is already equal to or smaller than the RL (TV $\leq$ RL), then it is not necessary to repeat the MDL study.

    2) The MDL should be less than the report level.

18. If the initial MDL study fails, the analyst should consult with the QAO before conducting a second MDL study at a different level. If the second trial fails, a third may be attempted. Indicate on the worksheet if this is the first, second or third MDL trial for that analyte.

19. A copy of the instrument raw data sheet(s) used to calculate the MDL must be attached to the worksheet. Each raw data sheet must indicate the target analyte, MDH LIMS code (or analyses name if the LIMS code is not applicable), and analyst's name and/or initials. The MDL worksheet should include all of this information along with the submission date. Submit the MDL study packet to the QA Office.

Note: For additional information on MDL, see Appendix B to 40 CFR Part 136 – Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11.

Formulas for the MDL Single Analyte Worksheet

(and included as part of the MDL Single Analyte Worksheet Instructions)

prepared by Jesse Fillmore, March 2007

A	% Recovery (Result #1):								
B	Mean:								
C	% Recovery:								
D	Std. Dev. (n-1):								
E	Student's t:								
F	MDL:								
G	TV/MDL								
H	TV/MDL between 1 and 10?								
I	Is MDL ≤ RL?								
J	= IF(I31="No","TV ≤ to RL?"," ")								
A	= D20/$H19*100								
B	= SUM(D20:D31)/H20								
C	= IF(H21="","",H21/H19*100)								
D	= STDEV(D20:D31)								
E	= VLOOKUP(H20,B36:C41,2,FALSE)								
F	= H24*H25								
G	= H19/H27								
H	= IF(H29<1,"No",IF(H29>10,"No","Yes"))								
I	= IF(H27>H18,"No","Yes")								
J	= IF(I31="Yes"," ",IF(H19<=H18,"Yes","No "))								
A		=Result/True Value							
B		=Result1+Result2+... .Result12/Number of Points							
C		=Mean/True Value							
D	**	=SQRT((((n*SUM(Result1^2... .Result12^2))-(SUM(Result1... ..Result12))^2))/n(n-1))							
F		=Standard Deviation*Student's T							
G		=True Value/MDL							
	**	Where n = number of results							

Appendix 10

Policy and Procedure for Initial Demonstration of Capability Study

for the Environmental Testing Units of the Public Health Laboratory Division, Minnesota Department of Health

Scope and Frequency: This policy and procedure pertains to inorganic and organic chemical analyses and radiological analyses; it is not applicable to microbiological analyses. An Initial Demonstration of Capability (IDC) Study must be performed for each new method, for each new environmental matrix, for each new analyte, for each new instrument and for each new analyst. For new analysts, an IDC must, as a minimum, include steps #1-4 below. All other situations would require that items #1-6 be performed. An IDC may also be required whenever there is a significant change in the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis. The Quality Assurance Officer (QAO), in consultation with the analyst and Unit supervisor, would make this determination. The Quality Assurance Officer may waive or modify the IDC requirement when it is not feasible to conduct an Initial Demonstration of Capability Study.

Requirements: The analyst must follow requirements for the performance of an Initial Demonstration of Capability Study cited in the reference method or applicable regulatory program for which the data are to be used. A project or client may also specify additional IDC requirements. If no such requirements exist, the analyst shall utilize the IDC procedure described below. For analyses that are part of the UCMR2 (Unregulated Contaminant Monitoring Regulation), the analyst must follow the procedure outlined in Section 6 of UCMR2 Laboratory Approval Manual, version 2.0, October, 2006.

The elements of an Initial Demonstration of Capability are as follows:

1) Initial Calibration: Perform an initial calibration using standards that will bracket the range of concentration found in samples and that will define the working range of the instrument/analysis. Enough standards must be used to show that the curve is linear or to clearly define any area(s) of the curve that may be nonlinear.

2) External Verification of Calibration: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within acceptable limits, otherwise remedial action is taken and the entire IDC is repeated.

3) Initial Precision and Accuracy: Analyze four reagent blanks spiked at the concentration of the calibration check standard or mid-range standard. Calculate the mean concentration and the standard deviation of the set. The percent recovery and the percent relative standard deviation (%RSD) must meet the criteria established in the SOP.

4) Demonstration of Low Background: Analyze at least one Laboratory Reagent Blank (LRB) to determine reagent or laboratory contamination. The LRB result must meet the criteria established in the SOP for on-going demonstration of low background.

5) Minimum Reporting Level: A minimum reporting level (MRL) (also known as Reporting Limit or Report Level) must be established.

6) Method Detection Limit (MDL) Study: A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B and following the current guidelines in "MDH Environmental Laboratory Detection Level Policy and Procedure." This can be completed in one analytical run when performing an MDL study as part of an IDC. The Quality Assurance Officer may specify a time frame for completion of the MDL study.

Documentation and other requirements: The acceptance criteria for each element of the IDC, and corrective actions that the analyst must take if the acceptance criteria are not met, must be described in the SOP. The frequency with which an IDC is conducted must also be included in the SOP. The IDC must include all of the steps in the analysis including sample preparation and processing. For purposes of this policy and procedure, an environmental matrix may include multiple matrices (example: drinking water and non-potable water may be grouped together), so long as each matrix is processed and analyzed in a similar manner as part of a single SOP. The written SOP must list all of the matrices for which it is applicable. Every analyte or analysis, for which an IDC is required, must have an IDC on file in the QA office. An IDC for each analyst must also be on file for each analysis they perform where an IDC is required.

Note: The effective date of this document is the date of the last signature on this document. On the effective date, this document becomes an appendix to the *Quality Assurance Manual for the Environmental Testing Units of the Public Health Laboratory Division.*

Appendix 11

Policy and Procedure for Report Level Verification

for the Environmental Testing Units of the Public Health Laboratory Division, Minnesota Department of Health

This policy and procedure pertains to inorganic and organic chemical analyses; it is not applicable to microbiological and radiological analyses. The Quality Assurance Officer (QAO) may waive this requirement when it is not feasible to conduct a Report Level Verification (RLV). The QAO may also modify the RLV procedure (example: modifications for a multi-analyte analysis) or accept other QC procedures in lieu of an RLV.

The analyst must follow requirements for the performance of a Report Level Verification cited in the reference method or applicable regulatory program for which the data are to be used. A project or client may also specify the Report Level Verification procedure. If no such requirements exist, the analyst shall utilize the Report Level Verification (RLV) procedure outlined in (1) below. The analyst, with the approval of the QAO and the Supervisor, may choose the Minimum Reporting Level Verification (MRLV) procedure outlined in (2) as an alternative Report Level Verification when they have determined that it is more appropriate.

1) Report Level Verification (RLV) Check: (MN Rules 4740.2100, Subp. 8.C.) One RLV check must be performed each time the instrument is calibrated; if the instrument is not calibrated with each use, then the RLV shall be performed monthly. The RLV can be performed one of two ways: 1) by analyzing a standard at or below the reporting level, or 2) by recalculating the standard at the report level that was used to determine the calibration curve for the instrument. The analyst must choose which of these two RLV procedures will be used for a given SOP. The RLV check sample is not required to be processed through the entire SOP; preparation steps such as digestion, extraction, etc. can be omitted. The percent recovery of the standard must be within limits established for each analysis or analyte by the Quality Assurance Officer. (Note: MN Rules state that the percent recovery of the standard must fall within ± 40% of the true value)

2) Minimum Reporting Level Verification (MRLV): The MRLV is described in the UCMR2 (Unregulated Contaminant Monitoring Regulation) Laboratory Approval Manual, version 2.0, October, 2006. One Minimum Reporting Level Verification (MRLV) sample must be analyzed daily to demonstrate that, for each analyte near the MRL, the measured recovery for each analysis or analyte is within limits established by the Quality Assurance Officer. (Note: UCMR2 states recovery must be within 50% to 150%, inclusive). The MRLV sample is a Laboratory Fortified Blank (LFB) that must: contain all method preservatives described in the method, contain each analyte of interest at concentrations at or below the MRL, and be processed through the entire method procedure (i.e. including extraction, where applicable).

Remedial action: If the percent recovery of the Report Level Verification standard is outside the acceptance criteria, the analyst must either: 1) repeat the verification check or 2) recalibrate and then perform the Report Level Verification check. If the repeat RLV is within acceptance criteria, or if the instrument recalibration results in a Report Level Verification check that is within acceptance criteria, the analyst may proceed with the analytical run. If the second verification check is not within acceptance

criteria, the analyst must either: 1) recalibrate the instrument and then perform the Report Level Verification check once again, or 2) perform the RLV at a higher concentration level. If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the report level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed report level check using the elevated report level until a new calibration curve and report level verification standard meet the acceptance criteria. Analysts using the MRLV procedure must follow the remedial actions described in the UCMR2 Laboratory Approval Manual.

Documentation and other requirements: The Report Level Verification procedure (RLV or MRLV), including the acceptance criteria, must be described in the SOP. The frequency of any RLV or MRLV must also be stated in the SOP along with action the analyst must take if the acceptance criteria are not met. Results of the RLV or MRLV check shall be recorded as directed by the Unit Supervisor or Quality Assurance Officer.

Documentation and other requirements for modified RLV/MRLV or alternative QC procedures: If the QAO has determined that an analysis should use either a modified RLV/MRLV procedure or an alternative QC procedure in lieu of an RLV/MRLV, this must be described in the SOP. The SOP must state the frequency of such procedures, the acceptance criteria and any action the analyst must take if the acceptance criteria are not met. Results of the modified RLV/MRLV check or alternative QC procedure shall be recorded as directed by the Unit Supervisor or Quality Assurance Officer.

Note: The effective date of this document is the date of the last signature on this document. On the effective date, this document becomes an appendix to the *Quality Assurance Manual for the Environmental Testing Units of the Public Health Laboratory Division.*

Appendix 12
USEPA Certification for Laboratory Analyses for Drinking Water

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 5
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

AUG 29 2008

REPLY TO THE ATTENTION OF

WG-15J

Dr. Louise Liao
Minnesota Dept. of Health
Division of Public Laboratories
601 Robert Street North
P.O. Box 64899
St. Paul, MN 55164-0899

Dear Dr. Liao:

On May 5-7, 2008, Patrick Churilla inspected your laboratory for proficiency in chemical, microbiological and radiochemical drinking water methods pursuant to the National Primary Drinking Water Regulations as implemented by 40 CFR Parts 141 and 142.

Based on the information obtained during the on-site visits to your laboratory and your responses to our draft findings, the United States Environmental Protection Agency grants to the Minnesota Department of Health, 601 Robert Street North, St. Paul, MN 55164-0899, full certification for the chemistry, microbiology and radiochemistry methods and parameters identified in Enclosure A.

If you have any questions or require clarification concerning this memo, please contact Patrick Churilla, at (312) 353-6175, by FAX at (312) 886-6171 or by E-mail at churilla.patrick@epa.gov.

Sincerely,

Thomas Poy

for Timothy C. Henry
Acting Director, Water Division

Enclosure

http://fyi.health.state.mn.us/phl/environmental/index.html

USEPA Certification for Laboratory Analyses for Drinking Water

ENCLOSURE A

LABORATORY CERTIFICATION SUMMARY
Minnesota Department of Health
(May 5-7, 2008)

Parameters/Method	Certification Status
1. Metals-ICP-AES/ 200.7 * Barium * Calcium * Copper * Iron * Magnesium * Sodium	Fully Certified
2. Metals-ICP-MS / 200.8 * Aluminum * Antimony * Arsenic * Barium * Beryllium * Cadmium * Chromium * Copper * Lead * Manganese * Nickel * Selenium * Silver * Thallium * Zinc	Fully Certified
3. Mercury-Cold Vapor AA /245.2, 1631	Fully Certified
4. Cyanide /SM 4500-CN F	Fully Certified
5. Alkalinity / SM2320B	Fully Certified
6. O-Phosphate / SM4500-P E	Fully Certified
7. Silica / SM4500-SiO2 C	Fully Certified
8. Fluoride / SM4500-F C	Fully Certified
9. Nitrate + Nitrite / SM4500-NO3 F	Fully Certified
10. Nitrite / SM 4500-NO2 B	Fully Certified
11. Disinfection Byproducts / 300.1 * Bromate * Chlorite * Bromide * Sulfate * Chloride	Fully Certified
12. Total Organic Carbon / SM5310 C	Fully Certified
13. Carbamates / 531.1 * Aldicarb * Aldicarb Sulfone * Aldicarb Sulfoxide * Carbaryl * Carbofuran * 3-Hydroxycarbofuran * Methomyl * Oxamyl	Fully Certified
14. EDB and DBCP/504.1 * 1,2-Dibromoethane * 1,2-Dibromo-3-chloropropane	Fully Certified

USEPA Certification for Laboratory Analyses for Drinking Water

Parameters/Method	Certification Status
15. Haloacetic Acids / 552.2	Fully Certified
* Bromoacetic Acid	
* Chloroacetic Acid	
* Dibromoacetic Acid	
* Dichloroacetic Acid	
* Trichloroacetic Acid	
16. Pesticides / 508.1	Fully Certified
* Aldrin	
* Alachlor	
* Atrazine	
* Butachlor	
* Dieldrin	
* Endrin	
* Heptachlor	
* Heptachlor epoxide	
* Hexachlorobenzene	
* Hexachlorocyclypentadiene	
* Lindane	
* Methoxychlor	
* Metolachlor	
* Metribuzin	
* Propachlor	
* Simazine	
* Toxaphene	
* Technical chlordane	
17. Herbicides / 515.4	Fully Certified
* 2,4-D	
* 2,4,5-TP	
* Dalapon	
* Dinoseb	
* Pentachlorophenol	
* Picloram	
18. Volatile Organic Chemicals/ 524.2	Fully Certified
* Benzene	
* Carbon tetrachloride	
* Chlorobenzene	
* Dichloromethane	
* 1,1-Dichloroethene	
* 1,2-Dichloroethane	
* cis-1,2-Dichloroethene	
* trans-1,2-Dichloroethene	
* 1,2-Dichloropropane	
* Ethylbenzene	
* Styrene	
* Toluene	
* Tetrachloroethylene	
* Trichloroethylene	
* 1,1,1-Trichloroethane	
* 1,1,2-Trichloroethane	
* 1,2,4-Trichlorobenzene	
* vinyl chloride	
* Xylene (total)	
* Total Trihalomethanes	
* Chloroform	
* Bromodichloromethane	
* Dibromochloromethane	
* Bromoform	
19. Glyphosate / 547	Fully Certified

USEPA Certification for Laboratory Analyses for Drinking Water

Parameters/Method	Certification Status
20. Other SOCs / 525.2	Fully Certified
* Aldrin	
* Alachlor	
* Atrazine	
* Benzo(A)Pyrene	
* Butachlor	
* Dieldrin	
* Di(2-ethylhexyl)adipate	
* Di(2-ethylhexyl)phthalate	
* Endrin	
* Heptachlor	
* Heptachlor epoxide	
* Hexachlorobenzene	
* Hexachlorocyclopentadiene	
* Lindane	
* Methoxychlor	
* Metolachlor	
* Metribuzin	
* Propachlor	
* Simazine	
* Toxaphene	
* Technical Chlordane	
* alpha-Chlordane	
* gamma-Chlordane	
* trans-Nonachlor	
21. Total Coliform, Fecal Coliform, E. coli /	
* Colilert - P/A Format	Fully Certified
* Membrane Filter SM 9222B and G2	Fully Certified
22. E. coli Enumeration /	
* Membrane Filter EPA 1103.1, SM9213D	Fully Certified
* Most Probable Number SM9223B	Fully Certified
23. Gross Alpha / 900.0	Fully Certified
24. Gross Beta / 900.0	Fully Certified
25. Radium 226 / 903.0	Fully Certified
26. Radium 228 / 904.0	Fully Certified
27. Uranium / 200.8	Fully Certified
28. Tritium / EPA600/4-75-008, March 1976, p34	Fully Certified
29. Strontium 89,90 / 905.0	Fully Certified
30. Photon Emitters / 901.1	Fully Certified
31. Radon / SM 7500-Rn	Fully Certified
32. SUVA UV Absorbance at 254nm	Fully Certified
33. Disolved Organic Carbon / SM5310C	Fully Certified

Appendix 13
Corrective Action Form for Non-conforming Work

Corrective Action Form (CAF)

Parameter(s) _____ CAF Number (completed by QAO): _____

PT Program (if applicable): _____ Issue Date (date of observed deficiency): _____

CAF Due Date (2 weeks after Issue Date): _____

A corrective action form is required when departures from the established quality assurance and quality control policies and procedures occur or in the event of a proficiency test (PT) failure. Non-conformance activities and PT failures require an investigation and documentation of potential causes and corrective actions. The analyst should complete the Corrective Action Form (CAF) within ***two weeks*** of recognizing the deficiency. The Quality Assurance Officer reviews and files the original submission, and monitors the corrective action progress and effectiveness.

Analyst/Investigator: _____ Report Value: _____

Sample Number(s): _____ True Value: _____

Analysis Date: _____ Control Limit Ranges: _____

Method/Instrument: _____ Acceptance Range (if applicable): _____

Description of Problem: *check those that apply*

___ An error in transcription, dilution, decimals, units, calculations and/or significant figures (*e.g.* compare instrument printout with result sheet and compare graded PT report with answer sheet for PT project)

___ The unapproved use or modification of an Standard Operating Procedure

___ Mishaps with sample collection, delivery, receipt, handling, identification, preservation and/or storage

___ Internal or external audit deficiencies

___ Instrument or analytical procedure not within Quality Control parameters (*e.g.* calibration records, standard expiration dates, and control limits)

___ Instrument and/or software malfunction with integration or data transfer (*e.g.* check QC parameters, preventative maintenance records, and instrument operations

___ Proficiency Test (PT) parameter failed to be within provider's acceptable limits

___ Other, please explain:

_____

Investigative Steps Taken: *see page 2 for possible investigative steps for unacceptable PT results*

Original: Quality Assurance Officer *Copy: S:\QA Records Env\Corrective Actions\2008 CAF*

Proficiency Test (PT) Investigative Steps Taken: *check those that apply*

___ Re-read the instruction sheets for the PT sample(s) to see if special instructions (time, handling, temperature, dilution, etc.) were overlooked.
___ Check the QC values for previous runs prior to performing the PT to detect any shifts or trends that may have affected PT results.
___ Check the calibration records, if applicable, to determine if it is time to recalibrate.
___ Check to see if there is an action log indicating problems prior to running the PT.
___ Check to see if there is any remaining sample and if so re-analyze.
___ Verify that the QCS associated with the calibration curve used for analyzing the PT was within range.
___ Other, please explain: _____

Operations/Data Affected:

Corrective Action Taken:

Results of Corrective Action/Data Corrected:

Acceptance Signatures of Corrective Action(s): **Print this form, sign and date, and route to:**

_____ Analyst/Initiator (signature & date)

_____ Unit Supervisor (signature & date)

_____ Quality Assurance Officer (signature & date)

_____ Laboratory Section Manager (signature & date)

Original: Quality Assurance Officer

Copy: S:\QA Records Env\Corrective Actions\2008 CAF

Minnesota Department of Health
Environmental Laboratory

Sample Acceptance Policy

The Operations Unit of the MDH Environmental Laboratory is responsible for the use and updating of this policy. In general, the staff attempts to resolve issues before the laboratory must reject a sample.

When we note a sample does not meet the conditions for acceptance for accurate testing, we will contact the responsible party for instructions. We define our minimum level of acceptability by the terms required in federal law, state laws and regulations, or agreements established for particular projects.

When we are not certain of the category for acceptance (CWA, SDWA, RCRA, etc.) for a particular sample (i.e. the collector did not provide the project identification or indicate specific tests), we will use the most stringent criteria to assure that the data are usable. For missing items not affecting the outcome of the analysis (e.g. collector name, collection year), we will leave the information blank or, in the case of the collection year, we will document the sample was collected within the past twelve months, a reasonable assumption. We will retain records of these discrepancies but will not contact you so please be sure you maintain your sampling logbook should questions arise.

The following items will prevent us from analyzing your samples and supplying valid results:

- The sample containers were broken in shipment or the containers are leaking.
- The samples were preserved, but they require no preservation for accurate testing.
- The samples submitted for volatile organics analysis have headspace (i.e. air bubbles larger than pea size).
- We did not receive enough sample volume to perform the tests you requested.
- The sample container cap is loose and allows extraneous water or materials to seep into the samples.

We consider the following items crucial to valid testing. We may be able to test the samples after we obtain more information from you. The samples will be placed on hold in our sample receiving area until our staff receives the necessary information and authorization from you to proceed.

- The paperwork submitted with the samples does not match the information on the sample container.
- The laboratory receives the samples after the method specified holding time.
- A sample submission form or chain-of-custody was not provided, or the form supplied is incomplete.
- The labels on the bottles do not have a unique identifier that matches a corresponding item on the form.
- We cannot read the sample labels.
- The collector did not use the correct sample containers for the tests requested.
- The samples were not maintained at the proper temperature to prevent deterioration.
- Legal chain-of-custody samples received with evidence of tampering (e.g., the custody seals are broken).

If you have questions or comments about this policy or about samples you have submitted to our laboratory, please contact our Operations Unit at 651-201-5300.

Environmental Laboratory
601 Robert Street N.
St. Paul, MN 55164
651-201-5300

MINNESOTA MDH DEPARTMENT OF HEALTH

Sample Receiving Procedure Manual

For the

Public Health Laboratory Division
Environmental Laboratory
601 Robert Street North
P.O. Box 64899
St. Paul, Minnesota 55164-0899

Revision Record			
Rev. #	Revision Date	Author/Reviser	Description of Change
4	10/17/06	Andrew Mittendorff	Updated for new building, LIM system changes

Approvals:

Andrew Mittendorff
Lead Worker, Sample Receiving

Laura Fischer
Supervisor, Laboratory Services

Gary Jones
Information Systems Manager

Stephanie Drier
QA Officer, Environmental Laboratory

TABLE OF CONTENTS

INTRODUCTION TO SAMPLE RECEIVING

CLIENTELE

The Minnesota Department of Health Environmental Laboratory receives samples from the following clients:

State Agencies (Listed in order of sample volume received):

1. Minnesota Department of Health Environmental Health Division
   Subdivisions (Sections):
   - Asbestos and Radiation Section
   - Drinking Water Protection Section
   - Environmental Health Services Section
   - Well Management Section
2. Minnesota Pollution Control Agency
3. Minnesota Department of Transportation
4. Minnesota Occupational Safety & Health Agency (OSHA)
5. Minnesota Department of Agriculture
6. Minnesota Department of Natural Resources

Federal Clients:

1. U.S. Forest Service
2. Pipestone National Monument
3. Army Corp of Engineers

Private Companies:

1. Northshore Mining
2. LTV Steel

PROGRAM CODES

Program/Client Specific Codes

Each client or program is assigned its own two-letter MDH Program Code, which is used for billing. We are unable to perform initial data entry without a program code. More detail about the program codes can be found in the client specific sections of this manual. Also, refer to the Environmental Laboratory Handbook for a complete list of program codes.

Miscellaneous Program Code

Program code **LN** is used for clients that we do not have a contract with. A billing name and address must be included with these samples. Some **LN** samples will also be accompanied by a check, which should be directed to the Assistant Lab Manager.

Laboratory Consult/Non-Billable Program Code

Program code **LM** is used for testing that is done internally for MDH and as described above, we do not bill ourselves.

Quality Control Code

Program code **LQ** is used for several different types of special samples. The Bio-Terrorism/ Chemical-Terrorism group uses it for emergency and QC samples they receive. It is also used for Proficiency Testing (PT) samples.

Environmental Health Codes

Most samples from Environmental Health use codes that start with the letter **H**. Some special programs will use an **I** program code.

Department of Transportation Codes

The DOT uses codes that start with the letter **D.**

Pollution Control Agency Codes

The MPCA uses codes that start with **P, Q, R** or **S** depending on the program.

DATA SHEETS

Data Sheets must accompany all samples submitted to the Laboratory. A wide variety of Data Sheets are used, but they should all include the Program Code, Analysis Codes, Collection Date, Etc. Each type of data sheet is described in more detail in the client specific sections of this manual.

GENERAL TASKS

Tasks to be performed in the morning
Check the refrigerator in Sample Receiving and the refrigerator in room L100 for samples that may have arrived after-hours.

Tasks to be performed throughout the day
Check email and voicemail as needed.
Process and deliver samples to the labs.
Bring data sheets and log lists to clerical periodically, so they receive a steady flow of work.

Tasks to be performed first thing in the morning on the first workday after any day(s) off
The weekend analysts leave the data sheets on the counter in Sample Receiving. Print a log list for the samples that were processed on the weekend or day(s) off.
Compare the data sheets with the log.
Make corrections to data sheets or initial entry data as needed.
If any samples were past hold time, check email for responses from clients. Check rejection pending list and make appropriate changes.

Tasks to perform at the End of Each Month
Prepare monthly report using sample receiving counts from Ed.
Add up bottle orders for the month and send report to Ron.

Tasks to Perform at the Beginning of Each Calendar Year
Reset the Rapidprint numbering machine to YYY00000 so the first number to print is YYY00001. The Y's represent the last three numerals of the current year. Example: For 2006, the machine was set at 00600000 so the first number to print was 00600001.

COMPUTER OPERATIONS

OVERVIEW OF SAMPLE ENTRY SCREENS

Log-in by opening the Sample Entry website, than enter your Username and Password. This initial screen is also used to change your password. Logging-in will bring you to a screen with several menu options. Operations not used by Sample Receiving are not included in this overview, although they may be available onscreen.

Bold, underlined text indicates a principal operation on the main screen.
Bold text indicates an operation that is accessed through the principal operation.
Italics text indicates second level menu options.
Bold Italics text indicates a field on the screen where information is entered by the user.

Editing

Initial entry: This is used to edit data that was entered on the initial entry screen. Up to 20 sample numbers can be edited at one time.
Default lists: This is used to edit the Program Code/Analysis Code default lists.
Ed Labels/bottle: This is used to change the number of labels that will print for each analysis code.

Entry

Initial Entry: This is used to perform initial data entry and to edit ***Trip Blank/Field Blank*** information.
Reject Pending List: This brings up the list of samples that have been placed in the rejection list. Based on responses from clients samples are checked either "Run Anyway" or "Reject".

Logs/Lists

Daily Entry Log: This is used to print the Sample Entry Logs that we compare to the data sheets before delivering them to clerical.
AN Analyte List: We use four of the selections under this heading. Once a list is selected, it will print automatically.
Bottle Type List: List of all bottle types and all of the analysis codes that are run from each type.
Assoc An List: List of all analysis codes that are associated with other analysis codes. When the listed code is assigned, the other code will automatically default in.
Def An by Prog: Lists by number all the default analysis lists that have been created for each program code.

View

Lab Review: This is used to look up data (including results) via the Sample #, PWS ID #, Collection Date, Collector, Program Code or AN Code.
PWS Table View: This is used to find PWS ID numbers, PWS names and addresses via the facility name, city, zip code, etc.

INITIAL DATA ENTRY PROCEDURE

Most computer functions can be performed by using the keyboard or mouse or a combination of both. The "Enter" or "Tab" keys are used interchangeably to move from one field to the next.

1. From the main screen select **Entry** and pull-down to select **Initial Entry**.

2. The cursor will be on the ***Beginning Sample*** # on the Initial Entry Screen.

3. Type in the 9-digit sample number, beginning with the year and then press Enter/Tab to go to the next field. (Example: 200612345)

4. The same sample # will default into the ***Ending Sample*** # field, but you can enter a series of samples together if they have the same program code, AN codes, and collection date. Use the arrow keys to move the cursor and type over the number(s) you want to change.

5. Press Enter/Tab key twice to get to ***Program*** (Received date-time will default automatically), and type in the two letter Program Code. The full name of the program should default into ***Client Program*** box at the bottom of the screen.

6. The next field ***List*** # is optional. For most routine samples, analysis lists have been created to make entering AN codes easier. Initially the list # will show the number "0". To use a default list, type in the chosen list number for that program and press Enter/Tab key. The analysis codes from that list will appear in the AN (analysis) column.
   If the "0" is left in the ***list*** # field, and the previous sample had the same program code, the previous samples analysis codes will automatically be entered. So if you are entering a series of similar samples with the same program code you can use list # 0 to repeat the same analysis codes.
   If you don't want to use a ***list*** # and the sample has the same program code as the one before it, you will need to use the mouse to move the cursor to the next field. If the program code is different than the previous sample, you can just Enter/Tab past this field and no analysis codes will be entered.

7. Enter ***Collection Date*** (if none enter ***Postmarked Date***). The system will use this date to calculate holding time for the sample.

8. Use the mouse to move the cursor to the ***AN*** field on the right side of the screen under the "Analysis Data" section. If a ***List*** # was entered, there will already be some analysis codes here. Otherwise, manually enter the appropriate analysis codes as shown on the lab request form.

9. Next to the ***AN*** field is the ***Priority*** field (***Pri***). If the lab sheet requests "Priority 1 Analysis" for the sample, change the "3" to a "1" in this field for each analysis code entered. This will automatically add a surcharge for the faster service.

10. There are additional fields that are also sometimes used:
    - ***Receiving Desk Comments*** field can be used to enter additional information about the sample(s). Comments written on the lab sheets will also be entered by the clerical unit.
    - ***Field Blank*** and ***Trip Blank*** fields are used to enter the sample numbers for field/trip blanks if they accompanied the samples. These are most often used for organic samples from the PCA. The data sheet will list the field/trip blanks and indicate which samples they are associated with. Trip blanks are filled with specially prepared water at MDH and are kept with the sample vials throughout the collection process. Field blanks are filled by the collectors and then are kept with the samples during collection. The lab compares the results of the trip/field blank with the sample results.

11. When all initial entry information has been entered, commit the record by hitting "F3" or clicking "Save" (yellow disk icon) with the mouse. The system will then determine if the analysis codes entered have short hold times.

12. If there is a short hold time you will be asked if you want to enter collection time. If this information is available on the sheet hit "yes" and it will take you to a Time Entry Screen. After entering the ***collection time***(s) the system will check if samples have passed their hold times. If so you will need to fill out the rejection email form to notify the collector/client the samples are past hold time. On this screen the important information to enter is ***PWS #*** or ***Location***, and ***Collector ID*** or ***Collector Name***. Once they receive the email they will have the opportunity to respond whether they want the samples rejected or run anyways.

13. After all information entry is completed a prompt screen will appear asking if you want to print labels now. Click on the appropriate box (Yes or No) or press the enter key to default to "No". It is often easier to print all labels together when you have finished entering a whole batch of samples.

REJECTION PENDING LIST PROCEDURE

When the LIMS system calculates that a sample has passed the hold time it will place it in the Rejection Pending List and ask the user to fill out an email form. The email will be automatically sent to the client(s) that are identified with the particular program code. The client then needs to reply to confirm the rejection or ask that the sample be run anyways.

1. From the main screen select **Entry** and pull-down to select **Reject Pending List.**

2. The screen will list all the samples that are pending. Next to each sample there are two boxes labeled "Run Anyway" and "Reject". Based on the clients response check the appropriate box. For samples that are rejected, the database will then indicate that they were past the hold time. For samples that are run, the database will indicate that they were past, but run anyways at the clients' request.

3. Bacteriological (An 327) samples that are between 30 and 48 hours will be put on the list even though we routinely run them anyways by a business rule with Environmental Health. For these samples both boxes will be checked.

4. After making changes click the "Confirm Rejection" box which will commit the changes and remove the samples from the list.

EDITING SAMPLE ENTRY INFORMATION

Sample entry information may need to be edited due to initial entry error or because the collector, laboratory or EH DWP employee have requested changes to the analysis codes, program code, etc. If you are making actual changes to the sample (not just correcting errors) be sure and add a receiving comment to the sample so there will be a record of all changes made.

Using the Editing: Init Entry Screen

When using this screen, you may edit up to 20 sample numbers at one time. You may change the ***Program Code, Receiving Comments, Analysis (AN) codes, Collection Date/Time, Priority*** and ***Priority Memo Date***.

1. From the main screen use the mouse to select **eDiting** and pull down to select **Init Entry**.

2. In the two boxes at the top of the screen, type in the first and last sample numbers for the samples that need editing. Up to 20 samples can be edited together as a group.

3. After the numbers are entered the system will pull up the information on the samples. The left side of the screen will show all the samples with the program codes. The right side of the screen will show the analysis codes, priority and priority memo date (if any) for the sample that is currently selected.

4. After making the necessary changes hit the F3 key or click on "commit" to save.

   - To change the ***Program Code*** for a sample, type over the current code.

   - Add or change the ***Receiving Comment*** by clicking on the field and typing. Hitting "shift-F3" will copy the comment from the previous sample.

   - To edit ***AN*** codes select the appropriate sample by clicking on the sample number on the left side of the screen to highlight it. The analysis codes will appear in the right side box. To add an analysis code, click on the ***AN*** column and arrow down to the last code entered. Hit F4 to add a box and type in the analysis.
     Repeat as needed.
     You have the option to add the codes to all sample numbers in the group. If this is desired hit "yes" when asked to do so by the system.
     To delete an analysis code, click on the code in the ***AN*** column and hit "shift–F9" or click on the "delete record" button to remove the code.
     You can only delete codes from one sample at a time.

   - Change the ***Priority*** on a sample by clicking on this field on the right side of the screen. The priority for each analysis code has to be changed separately.

- Edit the ***Priority Memo Date*** in the appropriate field on the right side of the screen. This should be the date when the memo requesting the priority status was received. This date is used to calculate the appropriate holding time.

- To edit ***Collection Date/Time*** click on the button near the middle of the screen. This will take you to another screen where the date and time can be edited.

Editing Field and Trip Blank information

This information can only be edited through the initial entry screen, and only one sample can be edited at a time.

1. Once inside initial entry, hit F7 or click on the "Enter Query" button at the top of the screen to put it in Query Mode.

2. Type in the sample number and then hit F8 or the "Execute Query" button.

3. This will pull up the information on the sample and allow you to edit the ***Field Blank*** and/or ***Trip Blank*** info.

4. After making changes, hit F3 to commit the changes to the database.

5. Repeat as needed to edit additional samples.

USING THE VIEW SCREENS TO FIND SAMPLE RECORDS

The View screens can be used to obtain missing sample information, look up results or search for specific samples. There are five options listed under **View**, but we only use the first and last options, **Lab Review** and **PWS Table View.**

Lab Review Screen

1. From the main screen use the mouse to select **View** and pull down to select **Lab Review**.

2. The screen will read "Data Review by", and will list four search options; ***Sample Number, PWS Number, Collect Date and Collector*** and ***Program, PWSN, Collected Date, etc***.

3. ***Sample #*** refers to the MDH number we assigned at login. Enter the number at the prompt and press the enter key to retrieve additional information. If the sample # is known, this is the quickest way to pull up the record. Once a sample record is retrieved you can check other samples in the sequence by clicking the "Prev Samp" and/or "Next Samp" buttons at the top of the screen.

4. ***PWS #*** is the Public Water Supply # assigned by Environmental Health. Enter the # at the prompt and press the enter key to retrieve additional information.

5. To use the ***Collection Date and Collector*** option you must know the collector's ID #. This is a four digit number that is assigned to each EH collector. Enter the ID# and press enter/tab to retrieve all sample records from that collector. A collection date can also be entered to narrow the search.

6. The final option ***Program, PWSN, Collected Date, etc*** allows you to search for samples using multiple criteria. This is the screen we use when searching for specific samples with little information to go on. Enter what information you have and leave the other fields blank. Click on "Fetch Data" or hit enter/tab from the last field to retrieve samples. This method can be useful when searching for samples for which we know the program and/or analysis codes.

PWS Table Review

This option is allows you to find a PWS number using the name or return address information. It also allows you to find the name and address information for a given PWS #.

1. From the main screen use the mouse to select **View** and pull down to select **PWS Table Review**.

2. Hit "F7" or click on the "Enter Query" button to put it in query mode.

3. To find the PWS # for a sample you can use the name and/or address fields to search for it. Enter the known information, using the "%" symbol to search for all systems with that word in their name. For example, querying %BAY% will bring up all systems with the word "BAY" in the name. Advance through the list using the arrow keys to find the right system. The other fields can also be used to search using the same method.

4. To find the address information, enter the PWS # and click on the "Execute Query" button. This will bring up the complete record for that system.

USING LAB REVIEW TO FIND A PROGRAM CODE

If samples are received with no program code indicated, the Lab review options can be used to figure out what the code should be. This method will only work for facilities that have a PWS ID #. If you do not know the PWS #, first use the PWS Table View screen to find it (see previous section).

1. From the main screen use select **View** and pull down to select **Lab Review**.

2. Using either the ***PWS Number*** or ***Program, PWSN, Collected Date, etc*** search options, enter the PWS # and execute a search. This should pull up all the sample records from that specific system.

3. Click on individual samples to pull up more information about the samples. Find the most recent sample with the same analysis codes and use that program code. It is important to find a previous sample with the same analyses because a system can have samples under different programs depending on the analysis codes.

4. If you cannot find the program code by following these steps, contact EH for assistance. If you are unable to obtain assistance before the sample must be submitted, choose the code that seems most appropriate. The code can be changed when you do obtain the correct information.

General Information on EH Program Codes
While the information below is helpful, always look up the facility information in the computer to determine the correct code (even for community samples).

HZ - SDWA Phosphorus study
HY - SDWA Lead/Copper
HJ - new well, Well Management groundwater quality
HM - private well water

Community PWS ID #s begin with a "1". Codes used are: **HA**, **HB** and **HC**. There will normally be more than one code per community as determined by sample type.
HA - community bacteriology samples
HB - community fluorides
HC - community code used for most other types samples

Non-community PWS ID #s begin with a "5". Codes used are **HD**, **HU** and **HW**. Some non-community facilities use more than one code. Contact the EH Rep for assistance in such cases as code assignment is not determined by sample type, but rather by facility type.
HD - non-community, licensed facilities
HU - non-community, non-licensed
HW - non-community, non-transient

ADMINISTRATIVE CODES

Administrative codes are used in the LIMS system to indicate various unusual changes to samples. The administrative codes that are used by Sample receiving are: **981, 993, 994, 995, 997 and 999.**

Codes 981 and 995- Samples Sent Out. These codes are added to samples when all or some of the requested analyses will be sub-contracted to another lab. They can be added during the initial data entry or after the fact through the editing screens.

Code 993- Analysis Canceled. This code is used when some or all of the requested analyses need to be canceled after they have already been logged in. This may happen if the submitter asks that some analyses be canceled, or if a problem is noticed in the lab that precludes testing.

- From the editing screen, add the **code 993** to the sample and delete the appropriate analysis codes. Add a receiving comment indicating which codes were removed, who requested the cancellation and the reason.

Code 994- No Sample Received. This code is used very infrequently to indicate that a sample indicated on a lab sheet was not received. Environmental Health uses mostly preprinted lab sheets for their sampling. In some cases not all the samples indicated on the sheets are collected. The well may be out of service or a sampling point may be inaccessible. Usually the collector will indicate in some way that the sample was not collected, by crossing it out or writing a note on the lab sheet.

- If this is the case just do not assign that particular sample point a number. **Code 994** should only be used in cases where there is no indication why a sample is missing.

Code 997- Number Not Used. This code is assigned to a sample number when the number was assigned in error and a correction to the data sheet is not possible. When an error is noticed we first try to correct it by moving the extra number to another sample or sheet. If no simply solution is possible, code 997 is used. See the next section for more information on correcting numbering errors.

Code 999- Analysis Can Not be Run. This code is assigned when a problem is noticed in Sample Receiving that would prevent the sample from being analyzed such as a broken bottle.

- During initial data entry, type in **code 999** instead of the affected codes, and a box will appear next to the AN code column.
- Double click on the box and enter the list of analysis codes that are to be rejected, separated by commas.
- This will bring up the rejection email screen, which is the sample screen used for samples that are past the hold time. To the lower left of the sample section is the Rejection Reason field. Several common sample problems are available as pull down menus, or other information can be typed in.
- Continue with entry as described in the Initial Entry Procedure section.

NUMBERING ERROR CORRECTION PROCEDURES

Numbers on a data sheet must be in sequential order, so if a number is stamped by mistake (or missed) we try to shift the numbers around to keep everything in order.

- If too many numbers were stamped on a data sheet try to move the extra number(s) to another sheet. Check to see if there are any unnumbered data sheets that the extra number(s) can be moved too. For example, if two extra numbers were stamped off and you find an unnumbered data sheet with exactly two samples listed on it, write the extra numbers on this data sheet.
- If not enough sample numbers were stamped on a data sheet it may be possible to add sequential numbers from the next data sheet. For example, if two more numbers are needed for a data sheet and the next data sheet has exactly two assigned numbers, write those two numbers on the first data sheet and renumber the second data sheet.

In some situations the numbering error cannot be easily resolved by shifting the numbers around.

- It is not possible to add a number to the data sheet because the sequential number was used on the next data sheet. Therefore all the sample numbers on the incorrect data sheet are extra.
- All the remaining data sheets have multiple sample numbers so the extra number cannot be reassigned to a single sample.

It is therefore necessary to create a new data sheet for the extra sample number.

- Using a new, blank MDH lab sheet, write the extra sample number(s) in the spaces at the top.
- Use program code **LM** for extra sample numbers.
- Write "**997- Number not used**" in the comments section.
- Enter code 997 for the sample(s).

If the error was noticed after initial data was entered it may be necessary to correct other sample information through the editing screens. Make sure that all samples have the correct program codes, AN codes and date/time.

Deliver the data sheets (including the one for code 997) and sample log list to the clerical unit as usual.

CHAIN-OF-CUSTODY

CUSTODY FORMS

"Chain-of-Custody" means that sample possession must be traceable from the time samples are collected until the samples or their derived data are used for enforcement purposes or are introduced as evidence in legal proceedings.

A Chain-of-Custody Form (C-of-C) must accompany the samples and all parties handling the samples must sign the form in the designated place (on the form) at the appropriate time.

There are several acceptable methods for submitting Chain-of-Custody samples:
1. The collector may use a MDH C-of-C in addition to their regular data sheet.
2. The collector may use the MDH C-of-C alone and write all of the necessary data on it.
3. The collector may use the Chain-of-Custody Form provided by their agency or company.

There are three custody status choices on the MDH C-of-C; ***Standard, Civil*** and ***Criminal***. Custody Forms provided by other agencies usually have the same three custody status choices. When samples come in accompanied by a C-of-C form, ask the collector if the samples are "Chain-of-Custody". The collector or submitter should select the appropriate option by circling it on the form, based on their desired level of custody.

Standard: This is for samples that do not require true Chain-of-Custody handling. Often the C-of-C form is used for regular sampling. The forms should still be signed, but there is no custody code to assign for such samples and they should be processed as normal.

Civil: This is for custody samples that may go to Civil Court. The collector or submitter has determined that there was no criminal intent or that it cannot be proven. Analysis code 990 should be assigned in addition to the requested AN codes.

Criminal: This is for custody samples that may go to Criminal Court. The collector or submitter has determined that there may have been criminal intent. Analysis code 991 should be assigned in addition to the requested AN codes.

C-of-C SAMPLE PROCESSING PROCEDURE

Sometimes C-of-C samples are sent in via courier in sealed containers. Check the seal to see if it is intact or not, make note of the status on the C-of-C form. If the seal is intact make a note of who cuts it. Sample Receiving personnel, Unit Supervisors and designated Management staff are authorized to handle custody samples.

1. Record the sample temperature using the IR thermometer in sample receiving. You can add a comment to the form such as "samples on ice" or "samples brought in immediately after collection" if the statement applies to the samples.

2. Follow basic sample processing procedures to check the Program Code, collection date/time, sample/data sheet identification match and analysis code/bottle type match. Resolve any discrepancies while the collector is still in Sample Receiving.

3. Have the collector sign the C-of-C form in the "Relinquished By" column.

4. Sign the form in the "Accepted By" column.

5. Give the collector the pink copy of the C-of-C form. If they also submitted a regular multi-copy data sheet, give them the pink copy of that as well.

6. After the submitter has signed off custody and the samples are determined to be acceptable they may leave. Once samples are in the possession of Sample Receiving personnel, they may not be left unattended. It is permissible to ask another Public Health Laboratory employee to watch the samples for a brief period of time.
A sample is considered to be in a person's custody if:
   - It is in a person's actual possession; OR
   - It is in view after being in a person's physical possession; OR
   - It was in a person's possession and that person locked the sample up in a secure cabinet or other storage container/facility.

7. Write the appropriate Chain-of-Custody code (990 or 991) on the C-of-C form and any other forms submitted with the samples. Depending on how the collector listed the samples, the custody code may not need to be added to each line of the form. Instead, it should be added only once per SAMPLING POINT.
   For example: If a submitter collected VOC and Metals samples from the same sampling point, but listed them on separate lines on the form, we would assign a separate sample number to each line but then assign the C-of-C code to only one of the sample numbers. If the custody code were assigned to both sample numbers, the submitter would be charged the custody fee twice for the same sampling point.
   Most collectors now list all bottles from a single sampling point on one line so this does not occur often, but it is still something we must watch for.

8. Write the C-of-C Unique Form Number (found on the upper right corner of the form) on all other forms submitted with the C-of-C form.

9. Follow basic sample processing procedures to number the samples, date/time stamp the data sheet and enter initial entry data in the computer. Be sure to enter the C-of-C code along with the test codes where appropriate (see step 8).

10. Attach the labels to the samples.

11. Separate the carbon copies of the C-of-C form and make a photocopy.
    - The original white form will go in the C-of-C binder in room L250.
    - The yellow copy will go to the submitting agency (usually the MPCA).
    - The photocopy will go to clerical.

12. If they also submitted a single copy data sheet make two photocopies of the data sheet.
    - Staple the original data sheet to the original C-of-C form for the C-of-C binder in L250.
    - Staple one copy of the data sheet to the yellow copy of the C-of-C form for the submitting agency (usually the MPCA).
    - Staple the other copy of the data sheet to the copy of the C-of-C form for clerical.

13. If they submitted a multi-copy data sheet.
    - Separate the copies and make a photocopy if necessary to equal three copies.
    - Then follow step 12.

14. Deliver the samples to the locked cooler in room L250. The key for this cooler is kept in the top left drawer by the numbering machine.

15. Place the original form(s) into the binder.

16. Carefully enter the samples into the Custody Logbook in room L250. Refer to previous entries if necessary for examples. Be sure to sign off custody when completed.

17. Let the appropriate laboratory units know that they received Chain-of-Custody samples. When Analysts are ready to perform the requested tests, they must sign the samples out through the Custody Logbook.

18. Print a daily entry log for the samples, verify all information was entered correctly and deliver appropriate copies to clerical.

19. Deliver copies to the submitting agency. For the MPCA samples place the sheets in the box on the counter for their courier to pick up.

PRIORITY LEVELS

Priority levels determine the length of time the laboratory has to analyze samples, from the time of receipt until results are available on the computer. Assigning the more urgent priority levels also automatically adds a surcharge to the sample analyses. The maximum analysis time for a given test at each priority level varies. Refer to the chart at the end of this section for more information.

There are four priority levels.

Priority 3: This is the routine priority level and is used for most samples. This priority level defaults in upon initial entry of sample data.

Priority 2: This priority level was used for some of the bottle blanks prepared by laboratory and laboratory services personnel. We do not currently use this priority level.

Priority 1: This is the priority level that submitters usually want when they request a faster turn around on samples. Most Priority 1 requests come from the PCA, but occasionally EH will ask for this priority as well. Priority 1 samples are assessed a 50% surcharge because they require special handling.

Priority 0 - Emergency: This is the highest priority level and usually is requested after consultation with the lab. A 150% surcharge is assessed if samples are accepted and analyzed during business hours. A 200% surcharge is assessed if samples are accepted and analysis is begun during non-business hours.

PRIORITY SAMPLE PROCEDURE

A request for expedited sample analysis should be made in writing. This can be written directly on the lab request or C-of-C form, or in a separate email, letter or fax. The memo should list all of the analysis codes that the submitter wants run at the high priority status. For Emergency samples, there should be an additional note on the memo or data sheet requesting Emergency status.

1. Write "**Priority 1**" or "**Emergency**" at the top of the data sheet.

2. Process the samples up to initial entry. During initial data entry you will need to change the priority level for each analysis code. In the ***Pri*** column change the "3" to a "1" or "0".

3. Press the F3 key to commit the data when you are finished.

4. Use the **eDiting** screen to enter the received date in the ***Priority Memo date*** field. This date is used to calculate the holding time for priority billing purposes. You can also change the priority status at this time if you forgot to do so during initial entry.

5. Attach the labels to the samples.

6. Make copies of the data sheet (and separate memo if necessary); one copy for each Unit Supervisor involved, one for Sample Receiving, and one for the Lab Manager. Also make extra copies of the data sheet to give to the lab analysts to help remind them of the priority status.

7. Deliver the samples to the appropriate labs making sure that the analysts are aware of the priority sample status.

8. Run a Daily Entry Log List for the priority samples and deliver it to clerical. Write "Priority" on top of the log sheet to ensure quick entry.

9. The Sample Receiving copy is kept in the file folder on the overhead shelf. The most recent should be put in the front of the folder.

Maximum Analytical Times/Priority Options Chart

	Priority 3		Priority 1	Emergency
	Water	Soil/Sed.	Water/Soil	Water
Bactichem				
Bacti only	2 days	---	2 days	24-36 hours
General Chem	21 days	25 days	7 days	72 hours
Metals	21 days	21 days	5 days	48 hours
Organics				
Volatiles	21 days	21 days	3 days	24 hours
Non-volatiles	21 days	25 days	5 days	48-72 hours
Radiation	25 days	25 days	7 days	72 hours

SPECIAL SAMPLE HANDLING

ORGANICS SAMPLES

- Make a copy of lab sheets for all VOC samples not collected by EH as part of regular monitoring. This includes samples from MPCA, and any other special projects. The copy is placed in the basket in the VOC room.

- Make a copy of lab sheets for all PFOS/PFOA samples and place it on the desk of Yongyi (Julia) Jiang.

- Make a copy of lab sheets for Organics samples other than routine samples collected by EH (analyses 407, 408, 409, and 415). The copy can be delivered directly to the appropriate analyst or placed with the samples in the cooler.

BACTI/CHEM SAMPLES

- Make a copy of lab sheets for all bacteriological samples other than 327s and deliver with the samples to the Microbiology bench.

- For Cryptosporidium samples (code 347), note the received temperature of the samples and make a copy of the sheet. Put the samples (either 10 liter jugs or plastic filter pipes) in the walk-in cooler in bactichem and place the lab sheet copy on the lab bench.

OSHA SAMPLES

Samples from OSHA are always program code MG, specific analysis codes can be found in the OSHA section later in the manual. The submitters will wait to leave until sample custody is signed over. Make a copy of all OSHA sheets. For organics samples deliver the samples with the original sheet and send the copy to clerical. For metals samples deliver the copy with the samples and send the original to clerical.

MICROPARTICULATE SAMPLES

We no longer analyze micro-particulate or asbestos samples at MDH. They are subcontracted out to Braun Intertec Labs. Most of the samples we receive for this type of analysis are from Northshore Mining. They send both air and water samples. They are supposed to notify David Foster before they send any samples. When they arrive let him know and he will fill out the special form and make the arrangements to send them out. Some of the samples have very short hold times so let David Foster know right away so he can get them processed.

SAMPLE RECEIVING EQUIPMENT

LABEL PRINTER

We use an **Epson LQ-870 printer** to print sample bottle labels. This printer is set up to print on 1" x 7/16" "piggyback" labels (in rows of 3 across). The labels are called "piggyback" because they have 2 layers of self-adhesive backing. A supply of these labels is kept in the MDH Stockroom, item #375-0503. There are 30,000 labels/box and we order 4-5 boxes at a time.

The correct ribbon for this printer is: **Nu-kote BM203 Epson LQ800**. A supply of these ribbons is kept in the MDH Stockroom, item #375-0716. We order 2-3 boxes at a time.

Installing labels in the printer:

1. Open the paper guides and slid the strip of labels up from underneath the printer head.
2. Turn the manual feed wheel to move the labels up.
3. Fit the labels over the paper guide grips and close the paper guides.
4. Line up the labels by carefully turning the manual feed wheel. The top of the clear plastic guard should line up between 2 labels (at the perforation).

Installing a new ribbon:

1. Make note of how the current ribbon is installed before removing it.
2. Put on a pair of disposable gloves to keep ink from staining fingers.
3. Remove the ribbon cartridge by pulling it out and then gently pull the ribbon from the guide.
4. Lower the new cartridge into place and guide the ribbon between the printhead and the guide.
5. Turn the knob in the direction of the arrow to remove any ribbon slack.

DATE/TIME CLOCK

We use an **Amano Cincinnati: PIX-3000 Electronic Time Recorder** to stamp the date and time on Data Sheets. Spare ink cartridges and the key to open the recorder are kept in the drawer right below it. To change the ribbon cartridge or to re-program the time, date etc., refer to the owner's manual.

To reset the recorder after a jam, unplug it and immediately plug it back in.

PHOTOCOPIER

We have a **Hewlett-Packard Model 280 Color Copier** in Sample Receiving. The Copier Manual and extra inkjet print cartridges are stored in the drawer just below.

Replacement inkjet print cartridges are available from the MDH Stockroom:
Black HP inkjet cartridges: Stockroom item #375-0025
Color HP inkjet cartridges: Stockroom item #375-0570

*Note: The color copy function no longer works. There appears to be a problem with the print head. However, since we don't make color copies this is not a problem.

FAX MACHINE

We have a **Brother Intellifax 4100 Laser Fax Machine** in Sample Receiving. It can also be used to make copies. The number is 651-201-5362 and it is shared with Clinical Accessioning.

SAMPLE RECEIVING MONTHLY REPORTS

The Sample Receiving Lead-worker is responsible for preparing monthly reports. The reports include the following information:

1. A per Unit (Metals, Organics, etc.) sample count for the month, along with the totals from the same month of the previous year.

2. Total number of samples received, all types (this is really the total of sample numbers used), along with the same total from one year before.

3. News of procedural changes, additions and other pertinent news.

After the report is completed one copy is emailed to the Laboratory Services Supervisor and a hardcopy is kept in the Sample Receiving Monthly Reports Logbook.

CREATING THE MONTHLY REPORT

The Monthly Sample Count is sent to sample receiving via email. This is a report of the total number of samples received, listed by Unit. On the report, Unit numbers are listed first, followed by a date, then the sample totals. The Unit numbers are assigned as follows per Unit (Metals, Organics, etc.) sample count for the month, along with the totals from the same month of the previous year.
0 = Administrative code (do not put in the report)
2 = Metals
4 = Organics
6 = Radiation
7 = Micro-particulate
8 = Bactichem

To find the total number of samples received in a month use the Lab Review function to find the first and last sample numbers used in the month. The total will be the Last sample number minus the First sample number plus 1.

Make note at the bottom of the report of any procedural changes, new programs or analysis codes or other important events that took place during the month.

HOLD TIMES LIST

TESTS WITH A ONE-DAY (24 HOUR) HOLD TIME

34 Chromium Hexavalent
54 UV Absorbance @ 254 nm
55 UV Absorbance @ 440 nm
302 MPN Total Coliform-P
304+ MPN Fecal Coliform-DW
305 MPN Fecal Coliform-P
309+ MF Fecal Coliform-DW Confirmatory
310* MF-Fecal Coliform
311* MF-E. Coli
312* MF-Enterococcus
313* MF-Fecal Strep

*Refrigeration to 4 degrees C is required for these codes and is recommended for all other microbiology samples.

Enforcement samples for fecal coliform and fecal strep (304, 305, 309, 310, 313) must be received within 6 hours of sampling. Any deviation from this standard must be okayed by the collector and/or the Bactichem lab. Make note of it on the comment line when entering initial data.

+All safe drinking water samples (DW) should be analyzed within 30 hours of collection. Any samples older than 30 hours, but less than 48 hours will be analyzed and the data flagged as possibly invalid. Make note of it on the comment line when entering initial data.

TESTS WITH A 2 DAY (48 HOUR) HOLD TIME

6 Solids, settleable
11 Turbidity
12 Color
35 Surfactant
63 Orthophosphate, total
67 Nitrite, total
69 Nitrate, UNPRESERVED w/ Yellow dot on cap
70 Orthophosphate, dissolved
73 Nitrite, dissolved
75 BOD (Bacterial Oxygen Demand), 20 day dissolved
76 BOD, 5 day dissolved
80 CBOD, 20 day NI Dissolved
81 CBOD, 5 day NI Dissolved
82 CBOD, 20 day NI
83 CBOD, 5 day NI
92 CBOD, 40 day NI
95 BOD, 20 day
96 BOD, 5 day
301 MPN total DW Coliform
315 Heterotrophic Plate Count (PP)
320 General Micro
327 E.H. Community (Program HA) PA-Coliform
330, 331, 332, 333, 334, 335: Various MPN Colilert tests

59/63 Combined in one 250 ml general bottle w/ yellow fill line. Program code HZ. Put the Total Phosphorus (59) label ON the bottle. Peel back 1/3 of Ortho Phos (63) label and place on the cap.

TESTS WITH A 3 DAY HOLD TIME

327 PA-Total Coliform-DW Colilert All types except for E.H. Community (HA Program)
308 MF-Total Coliform-DW

TESTS WITH A 4 DAY HOLD TIME

809 Radon

TESTS WITH A 5 DAY HOLD TIME

807 Radium 226/228 (formerly test codes 805 & 806)
816 Gross Alpha, SDWA
SDWA Radiation samples must be acidified within 5 days of collection.

TESTS WITH A 7 DAY HOLD TIME

1 Solids
2 Solids, total volatile
3 Solids, suspended
4 Solids, suspended volatile
5 Solids, total dissolved
88 Sulfide
283 pH in sediment
402 SVOC's in water by GCMS (BNA)
410 Dalapon SDWA
411 Haloacetic Acid ICR
420 PCB Aroclors in water
470 PAH in water by HPLC
474 DRO in water
476 DRO in sediment
500 PCB (oil)
510 PAH in water by GCMS
512 PAH in water by GCMS/SIM

TESTS WITH A 14 DAY (2 WEEK) HOLD TIME

22 Alkalinity, total
26 Cyanide, Free SDWA
69 Nitrate Drinking Water
86 Cyanide, total
90 Cyanide, amenable
406 Herbicides
407 BNA's by GCMS, SDWA
409 Glyphosate
412 Haloacetonitriles
413 Chloral Hydrate
462 VOCs, special
463 VOCs & Gas/fuel
464 THMs
468 VOCs
473 GRO in water
475 GRO in sediment
498 VOCs White Caps
UNPRESERVED METALS (Including Copper/Lead)

TESTS WITH A 28 DAY (4 WEEK) HOLD TIME

14 Conductance @ 25 degrees C
23 Chloride, total
27 Sulfate, total SDWA
28 Sulfate, total, turbidimetric
29 Fluoride, total
30 Silica
37 Fluoride, dissolved
46 Chloride, dissolved
48 Sulfate, dissolved
49 Sulfate, dissolved, turbidimetric
50 Silica, dissolved, reactive
59 Phosphate total
60 Phosphate dissolved
64 Ammonia Nitrogen total
65 Organic Nitrogen total
68 Kjeldahl Nitrogen total
69 Nitrate
74 Organic Nitrogen dissolved
77 Ammonia Nitrogen dissolved
78 Nitrate dissolved
79 Kjeldahl Nitrogen dissolved
85 Phenol
94 COD (chemical oxygen demand) dissolved
97 COD total
98 TOC (Total Organic Carbon)
99 Dissolved Organic Carbon
200 Mercury, low level total in water
202 Mercury, low level dissolved in water
294 Perchlorate
403 EDB & DBCP, SDWA
408 Carbamates
452 Chlorophyll A, lab filtered
637 Mercury, SDWA
698 Mercury, high level total in water
699 Mercury, high level dissolved in water

TESTS WITH A 30 DAY HOLD TIME

450 Chlorophyll A, field filtered
451 Pheophytin A

TESTS WITH A 6 MONTH HOLD TIME

Preserved metals (except mercury)

ENVIRONMENTAL HEALTH SAMPLES

Environmental Health Public Water Supply samples must be handled in accordance with Environmental Protection Agency drinking water rules and regulations. The Environmental Health Division is organized as follows:

Division: Environmental Health

Section: Drinking Water Protection

Units: 1. Community Public Water Supply
Sub-unit: Corrosion Control

2. Non-Community Public Water Supply

3. Source Water Protection*

EH-PWS IDENTIFICATION NUMBERS AND PROGRAM CODES:

All EH-PWS samples are assigned a 7-digit Public Water Supply Identification Number (PWS ID #).

COMMUNITY PROGRAMS: PWS ID numbers begin with "1".
Program Codes used for Community samples are: HA, HB, HC & HY.

CORROSION CONTROL PROGRAM: PWS ID numbers can begin with 1 or 5 (even though this is a Community sub-unit). The only Program Code used is HZ.

NON-COMMUNITY PROGRAMS: PWS ID numbers begin with "5".
The Program Codes used for Non-community samples are: HD, HU, HW and HY.

* We rarely receive samples from this unit. The Program Code is IB and they do not use PWS ID numbers (because they are not public water supply samples).

EH-PWS Unit Program Codes:
HA: Community Water Supplies - Bacteriology
HB: Community Water Supplies - Fluoride
HC: Community Water Supplies - Sanitarian Managed
HD: Non-Community: Licensed, Transient*
HU: Non-Community: Non-Licensed, Transient*
HW: Non-Community: Non-Transient**
HY: SDWA Lead-Copper (Community and Non-community)
HZ: SDWA Corrosion Control

COMMUNITY SYSTEMS:
These public systems usually serve a variety of clients, i.e. one system may serve homes, schools and businesses. However, some systems serve only one Mobile Home Park or apartment building. The system operator usually submits the bacteriology, fluoride, nitrate and other routine samples while MDH Sanitarians collect non-routine samples.

NON-COMMUNITY SYSTEMS:
These private systems usually serve one facility, and they are usually smaller than community systems. However, it is possible for a large factory (private) to serve more clients than a Mobile Home Park (public). The system owner usually submits routine samples while MDH Sanitarians collect non-routine samples.

***Transient** means that individuals use the system no more than 8 hours/day (on average). If the facility is a business, it has no more than 25 employees.

****Non-transient** means that individuals use the system more than 8 hours/day. If the facility is a business, it has more than 25 employees. The same population uses the facility on a daily basis.

The HD Program Code is assigned to licensed facilities with short-term (transient) use. Examples are: resorts, campground, golf courses, restaurants and supper clubs.

The HU Program Code is assigned to non-licensed facilities with short-term use. Examples are: churches, parks, wayside rests and small businesses.

The HW Program Code is usually assigned to non-licensed facilities with long-term (non-transient) use. Examples are: schools, daycare centers, factories and larger businesses.

ENVIRONMENTAL HEALTH DATA SHEETS

MDH DATA SHEET

This type of data sheet is used to submit most samples collected for the Environmental Health-Public Water Supply Unit.
The following is a description of each section of the form.

1. **Program Code**: This is used for billing purposes.

2. **PWS ID #:** This is required for all samples submitted for Environmental Health Public Water Supply samples. If there is no PWS# on the form, you can look it up on the computer through Lab Review.

3. **Facility Name**: If no facility name is given, you may look it up on the computer by using the PWS ID# through Lab Review.

4. **City, Town, Township:** These can be looked up via the same method as the Facility Name.

5. **Date Collected:** This information is essential because we must know if the sample is valid. See section on Basic Sample Processing for instructions on handling samples that are submitted without collection dates.

6. **Time Collected:** This information is important for samples with short hold times.

7. **Collector ID** and **Collector Name**: The collector should fill in this information.

8. **Original Sample Number** and **Field Blank Number:** These fields are not necessary to process samples.

9. **Sample type**: If this information is missing, do not choose a type unless you are absolutely sure of the correct one. EH personnel will make corrections when they receive the lab report.
   - **O= Original/Routine**: All scheduled routine samples fall into this category.
   - **R= Repeat**: This type should be used for bacteriology repeat samples only.
   - **C= Confirmation**: This type should be used for nitrate confirmation samples only.
   - **I=Investigative**: This type should be used for all samples collected as part of follow-up investigation of positive or MCL violations.
   - **X=Other**

10. **Field Number**: This number is assigned by the collector to a given sample. For example, if a collectors initials are A.B.C. they might assign their first sample of the quarter the number ABC-001.

11. **Location ID**: there are 2 types of location ID's:

E = Entry point: This is used for Nitrate, Nitrite and most other samples (such as IOC, VOC and SOC).
D = Distribution: This is used for Bacteriology samples, some Fluorides and Radiation samples.
If there is more than one entry point and/or distribution at one facility, the collector will assign numbers along with the letter code. For example: E01, D01, E02, D02.
Because the Nitrate/Nitrite and Bacteriology samples are collected from different locations, they must be listed in separate columns on the data sheets. Usually, the Entry point is listed in the first column and the Distribution is listed in the second column.

12. **Sampling Point**: This is the site the collector obtained the sample from. Examples are: Women's bathroom tap, Kitchen tap, Well #1, Well #2, etc.

13. **Test Codes**: the collector will check the requested test codes in the appropriate columns.

14. **Lab Comments**: Collectors sometimes write sampling comments in this space. We can also use it to write brief comments about problems with the samples.

EH SAMPLES FROM NON-MDH COLLECTORS

There are specialized versions of the MDH #1 data sheet that are sent out to systems to collect their own samples. The Sheets are color coded and edited to make it easier for them.

HA Bacteriology form: The program code HA and sample type "O" are preprinted on this form. The 327 test code is highlighted and an "X" is preprinted in column one by the code. Other test codes are blacked out. Only one sample is collected from each facility per sampling cycle. The form and label are pink.

HB Fluoride form: The program code HB is preprinted on the form. The 29 test code is highlighted and an "X" is preprinted in column one by the code. Other test codes are blacked out. Only one sample is collected from each facility per sampling cycle. The form and label are blue.

HC Nitrate form: The program code HC is preprinted and test code 69 is highlighted but there may or may not be a preprinted "X". Multiple samples may be collected from one facility. The form and labels are green.

HC Arsenic form: The program code HC is preprinted and test code 110 is highlighted but there may or may not be a preprinted "X". Multiple samples may be collected from one facility. Code 601 (lab preservation) needs to be added for these samples. The form and labels are yellow.

SAMPLE PROCESSING PROCEDURE

SAMPLE DELIVERY SCHEDULE

Samples are delivered via the following schedule Monday-Friday. Times are approximate and each company normally delivers only once per day:

U.S. Mail	8:00 - 8:30 AM
United Parcel Service	9:00 - 10:00 AM
Spee-Dee Delivery	9:00 - 10:00 AM
Federal Express	Times vary, may not deliver every day

The U.S. mail is also delivered on Saturday, some Holidays and occasionally on Sunday (on Holiday weekends). The other courier services do not deliver samples on Saturday, Sunday or Holidays.

Individual collectors may bring in samples at any time of the day. They may also bring them in after hours if necessary. Samples brought in after hours should be placed in the Sample Receiving refrigerator or the after-hours refrigerator in room L100.

Opening Mailing Containers
Open boxes and other mailing containers carefully. You may need to use a retractable blade "Exacto" knife to open some boxes. It is advisable to wear safety glasses while using a knife.

Do not discard a box until you make sure a data sheet has been included with the sample and that it contains all of the necessary information*. If we receive a set of several boxes from one facility, open them at the same time. The data sheets for all of the grouped boxes may be sent in just one box.

*If there is no data sheet, see Step 4 for directions.

CHECKING BOTTLES FOR IDENTIFICATION

MAKE SURE THERE IS SOME TYPE OF IDENTIFICATION ON THE BOTTLES, such as facility name, PWS ID# or field number. If this information is missing, follow the directions below.

For samples collected by agencies other than MDH/EH, try to contact the collector directly. This includes MPCA, MN/DOT, OSHA etc.

For unmarked EH samples from a single sampling point:
Write the PWS ID# or facility name on the bottle(s) for the following types of samples: HA Bacteriology samples, HB Fluorides, HC nitrates sent singly, or any EH sample set/data sheet received in its own box (so we know it is from that facility only).

For unmarked EH samples from multiple sampling points:
Occasionally, groups of samples will be sent in from one facility with multiple sample points but the sample points or field numbers are not marked on the bottles. If the samples were all collected on the same day and the same test is being requested, randomly choose a bottle for each sampling point. Write the following comment on the data sheet (for each sample number involved): "No ID on bottles randomly chose one bottle for each sampling point". Write your initials by the comment so the clerical unit knows they need to enter the comment during secondary entry.

If you are at all unsure about the samples, follow the directions below:

- If the samples were collected by an EH collector, contact the person directly.

- If the samples were collected by the facility or by a contract collector (such as a county) that we do not have direct access to, contact the appropriate EH Program Representative(s). Send an email message to the appropriate group of people from the contact list.

Compare Data Sheets with the Samples Submitted
Make sure the field numbers, location ID's and sampling points on the forms correspond with the info on the samples.

If the information does not match:
Change the data sheet to correspond to the info on the bottles.
Using a red pen, cross out the data sheet info and write in the new info.
On Lab Comment line write: "Sampling point altered".

Determine that the Correct Bottles were Submitted
Check the Analysis codes requested to be sure that all of the correct bottles have been submitted. Refer to the bottle-type charts to make your determinations.

If you determine that the wrong bottles have been submitted, some substitutions can be made:
Non-thiosulfate Bacteriology bottles can be used for fluoride, nitrate, nitrite and sulfate.
General bottles can be used for nitrate, if sample is 2 days old or less.
Nutrient bottles can be used for nitrate (this is routinely done by the MPCA).
Free Cyanide and Total Cyanide bottles are interchangeable if there is adequate sample volume.
Other substitutions may be possible, check with the lab when incorrect bottles have been submitted.

In all cases above, check with the laboratory before submitting the sample and write a receiving comment that briefly describes the bottle substitution.

Bacteriology samples must be submitted in a sterile bottle, preferably our own Colilert, Thiosulfate or Non-Thiosulfate bottles. Occasionally, a collector may submit a bacteriology sample in their own sterile bottle, and this is usually acceptable, but check with the laboratory before submitting.

If the bottle submission problem cannot be resolved:
Notify the collector or appropriate EH Rep via phone or email. List the analyses that cannot be run and why.
If some of the analyses can still be run, cross out the codes that will not be run. Make note of the cancelled analyses and the date the collector was notified under "Receiving Comments" on the data sheet.

NUMBERING THE SAMPLE DATA SHEETS

Use the Rapidprint Machine to number the samples.

On the MDH #1 data sheet, there are 4 spaces across, corresponding to 4 columns. Make sure the numbers are stamped in corresponding fashion. For example, if samples are listed only in columns 3 & 4, stamp numbers in spaces 3 & 4 only.

On some types of data sheets we must also write the sample number(s) in designated places after stamping all of the numbers on the top. This includes the C-of-C forms, Radiation data sheets, OSHA forms, etc.

Some data sheets have columns or rows for 10-20 samples; we cannot stamp all of the numbers across the top of this type of sheet.

1. Stamp the first number; write "thru" or "through" after it.
2. Write the sample numbers in the designated spaces on the data sheet.
3. Use scratch paper to punch off additional number.
4. Stamp the last number of the sequence on the slab sheet.

Stamping the date/time on Data Sheets
Use the AMANO PIX 3000 Electronic Time Recorder (Time Clock) to stamp the date and time on the upper right corner of the data sheets. Do not stamp over a sample number or other pertinent information. Make sure that every sheet gets the Date/Time stamp so we can prove when the samples were received.

SAMPLES SUBMITTED WITHOUT A LAB SHEET

Occasionally samples are received without a lab sheet. We first try to fill out a sheet in Sample Receiving using information that may be on the mailing carton or bottle. To do this you must have at least a PWS # or location and be able to determine what type of sample analysis it is supposed to be for. If it is unclear what it is for or if there are other problems in filling out a lab sheet, email the Community or Non-Community groups in Environmental Health.

1. Use what ever information may be provided on the bottle or shipping container to look up site information from the LIMS (see section on Lab Review Screens).

2. As you obtain information, record it on an MDH Lab sheet. The minimum information needed to submit a sample to the laboratory is as follows:
   - Program Code
   - PWS ID# or Facility Name
   - Collection date or postmark information
   - Analysis Code(s)

3. If you can not figure out enough information to submit the sample contact an EH representative for assistance.

LABELING THE SAMPLE CONTAINERS

Most bottles we use now are single-use disposable bottles. For these bottles we can place the whole label on the bottles. We still use some bottle types that are washed and reused multiple times. For these bottle types (Fluoride, Nitrate, Cyanide and Microbiology), we need to peel back 1/3 of the backing on both sides of the label and fold the backing toward the middle of the label. Place the label on the bottle so that only the sides of the label adhere to it. This makes it easier to remove the labels for cleaning.

Refer to the data sheets as you label to ensure labels are placed on the correct samples.

If bottles are wet, wipe them off with disposable towels and/or use rubber bands to hold the labels in place.

The labels will print out grouped by bottle type. The upper right label for each group should describe which bottle they are for.

Special Sample Bottle Labeling

BOD/CBOD samples: As part of the processing of these samples the lab will submerge them in water, so the regular labels will not work. Using a black sharpie permanent marker, write the sample number on a 1 x 2-1/2" white shamrock label. Place this label on the shoulder of the bottle and deliver the printed labels along with the samples to the lab.

Chlorophyll/Pheophytin filter: Unwrap the filter(s) and make sure the filtered volume is written on the petri dish. If it is not, check the data sheet for this info and write it on the dish. If the volume is not on the data sheet either, call the collector. Place one label with just the sample number (no test code) on the petri dish containing the filter. Do not cover any information written on the dish. Re-wrap the filter or group of filters in foil. Place another label with sample number only on the foil. For a group of samples, use a label from the first and last numbers only; it is not necessary to put a label from each number on the foil. Clip all of the labels from one group together and save them for delivery to the lab.

Total/Ortho Phosphate samples: These samples are collected by community systems on behalf of Environmental Health. They are collected in an unpreserved nutrient bottle. Put the Total Phosphorus label on the bottle as normal. For the Ortho label, peel back 1/3 of the backing and stick it to the cap.

Multiple program samples: Occasionally the MPCA will submit samples that they want analyzed under two different programs. The sheets are given separate numbers and the labels are attached similarly to phosphate samples. One programs label on the side of the bottles and one on the top.

Metals bottles: Place the entire label on the bottle. Peel off one label with just the sample number and place on top of the bottle cap. The metals lab holds samples for several months.

Having the numbers visible from the top makes it easier for them to find samples on their carts

Organics bottles: Place one small label with the sample number and test code on the upper part of the bottle or vial. Most organic analyses will have their own bottle so the lab doesn't need the rest of the labels.

Radiation samples: Place one small label with just the sample number on the samples and save the rest of the label for delivery to the lab. For samples that have a paper tag, put the label on the tag.

Duplicate sample containers: Sometimes collectors will submit more than one of the same type of container for a sample. In these cases write "1 of 2" or "2 of 2" on a single label and put it on each container. Attach the rest of the labels to one of the containers or deliver them to the lab separately as needed.

OSHA samples: Do not remove the samples from their bags (the labs will do this). Just clip the labels and paperwork to the bag containing the samples. People in the labs will deal with labeling themselves.

PRINTING SAMPLE ENTRY LOG AND COMPARING TO DATA SHEETS

After samples have been delivered to the lab print a Daily Entry Log and compare it to the data sheets.

1. From the main screen select **Log/lists** and pull-down to select **Daily Entry log**.

2. Type in the beginning and ending sample numbers for the lab sheets.

3. Select the printer "Labserv 2" to print the log list.

4. The log will list all the sample numbers with some basic information about each one. The information we are checking for is: ***Program Code, Analysis Codes, Priority,*** and ***Field/Trip Blank***. As you are checking the samples, draw a line along the log list to indicate to Clerical staff that the log has been verified.

5. If there are any errors make changes using the edit screens and note the changes on the log list. If any analysis codes were entered incorrectly it is necessary to reprint the corrected labels. Find the sample bottles in the lab and attach the correct labels.

6. When you are finished paper clip the log list on top of the stack of lab sheets and deliver it to clerical. There is a basket for incoming work in the filing room.

DELIVERING SAMPLES TO THE LABORATORY

Deliver samples with short hold times first and notify lab personnel. It may be helpful to load samples onto the transport cart in the same order that they will be needed in the labs. Refer to the following descriptions for the correct ordering method.
Refer to the **Labs Map, South** for the following sample delivery locations.

C-of-C Room: All Chain of Custody Samples must go in the locked cooler in this room. The C-of-C log book is also located here.

1. Place ***radon*** samples in racks on this counter.

2. Place all other ***radiation chemistry*** samples on this lab counter and put extra labels in the basket. If it is late in the day and no one is in the radiation area put milk, crops, or other perishable samples into the fridge (**2a**).

3. Place all ***metals*** samples on this counter. Put samples in order left to right and front to back. Line up Metals samples and Mercury samples separately. Put any non water samples just to the right.

4. This is the preserved samples bench. There are trays for three different sample bottles; ***cyanide, nutrient*** and ***nitrate***. All bactichem samples should be lined up in order, left to right and back to front (except as noted). When a tray is full (or the tray is missing) more can be found in the cabinet just below the counter.

5. There are two trays on this counter. ***Nitrite*** samples go on the tray to the right, ***fluoride*** samples go on the tray to the left. The lab only runs fluorides every few weeks so the samples tend to accumulate. When a tray is full put a new tray on top and continue to line up samples as before.

6. This is the ***general*** (unpreserved) samples counter. There are not specific trays since many different types of samples and bottles are placed here. Try to keep similar samples grouped together as much as possible. In addition to samples collected in general bottles, any sample that is unpreserved should go on this counter. ***BOD/CBOD*** samples are placed on this counter, with the printed labels paper clipped together and sitting on top of the bottles for the lab analysts. The baskets for chlorophyll labels are located on this counter, just to the right of where the samples are put.

7. Put ***chlorophyll filters***, wrapped in tinfoil in this freezer; labels go in the (field-filtered chlorophyll) basket on the general counter (**6**).

8. Put chlorophyll bottles in the walk in cooler. Line them up on the shelves in the back left corner. Labels go in the (lab-filtered chlorophyll) basket on the general counter (**6**).

9. ***Cryptosporidium*** filters or water jugs go on the middle shelf just inside the cooler door.

10. ***Bromate/Chlorite*** samples should be collected in 250ml unpreserved plastic bottles, wrapped in tinfoil. Place them on the middle shelf in the cooler.

11. All ***bacteriological*** samples are placed on this counter. Line up samples in groups of five, front to back and right to left. For non routine bacti analyses, put copies of the lab sheets on top of the samples for the lab analysts.

12. Put copies of ***cryptosporidium*** lab sheets on this counter.

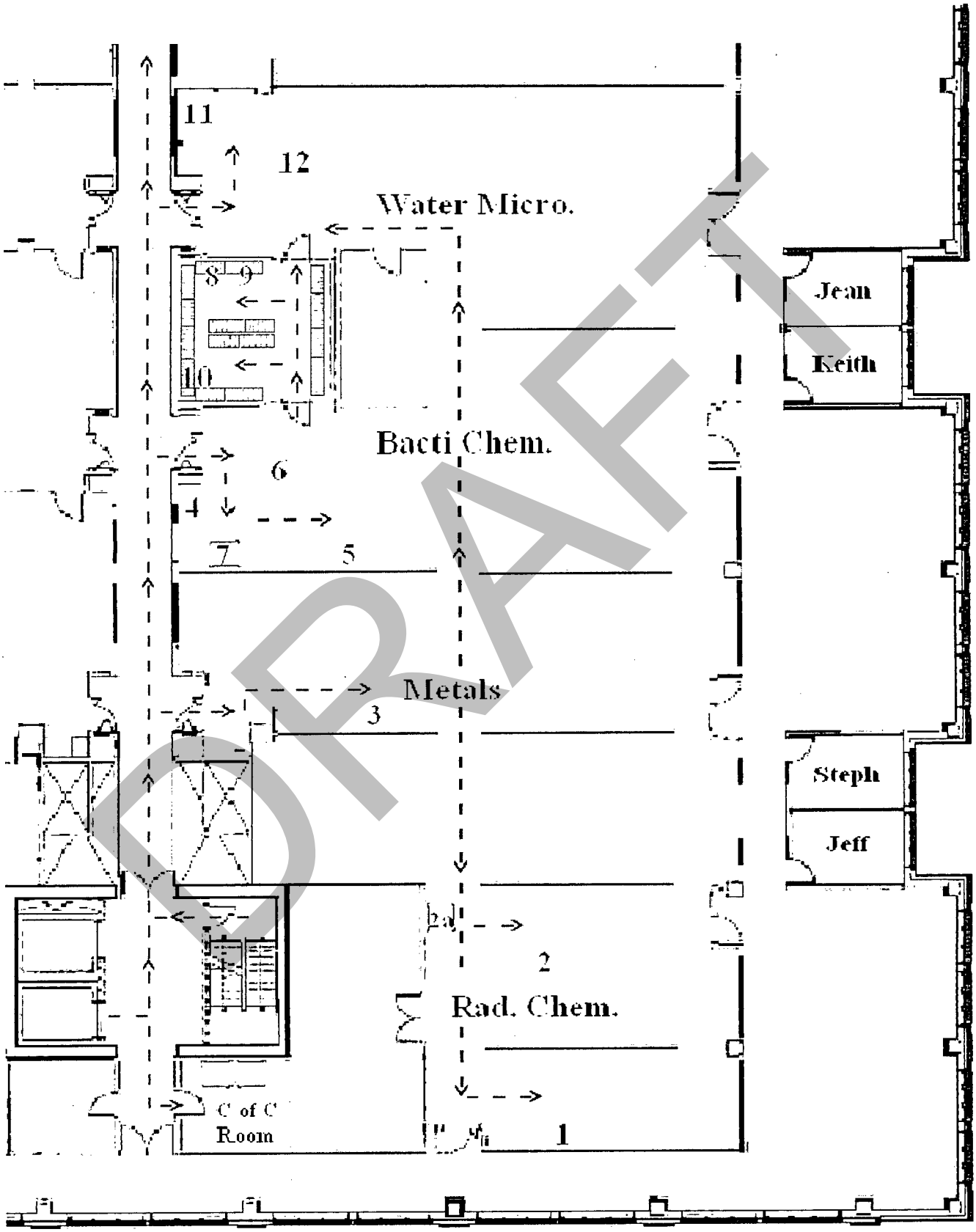
Refer to the **Labs Map, North** for the following sample delivery locations.

1. Most non-volatile organics samples, (***PFOS , SOC, PCB, SVOC, etc***) are placed in this refrigerator. This cooler is often quite full, but try to follow the shelf labels for the correct placement of samples. For PFOS samples, put a copy of the lab sheets on Julia's desk. For other non-routine samples, leave a copy of the lab sheet with the samples in the cooler.

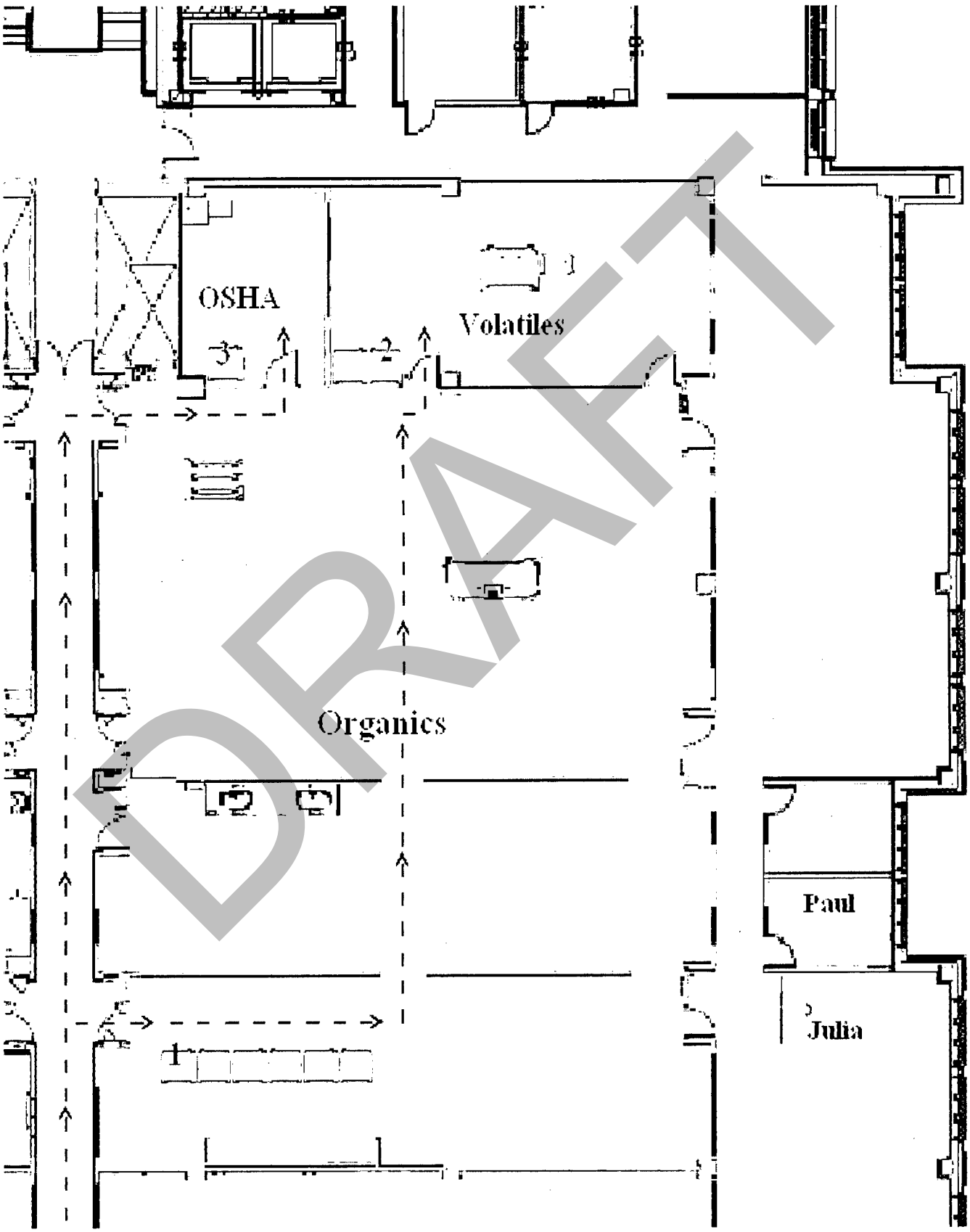
2. ***All volatile organics*** samples go in this fridge. The top two shelves are for 468 VOCs, the lower shelves are for 498 VOCs. Lab sheet copies go in the basket just opposite the cooler.

3. ***OSHA organics samples*** go in the locked half-size cooler in this room. Paperclip the bagged samples, labels and original lab sheets together and place in the cooler.

LABS MAP, SOUTH


11
12
Water Micro.
8
9
10
Jean
Keith
Bacti Chem.
6
4
7
5
Metals
3
Steph
Jeff
2a
2
Rad. Chem.
C of C
Room
1

LABS MAP, NORTH



MINNESOTA POLLUTION CONTROL AGENCY (MPCA) SAMPLES

The MPCA collects a great variety of samples from numerous locations around the state. They submit water samples from lakes, streams, rivers, feedlot run-off, closed landfill monitoring wells, drinking water (rarely), Superfund sites, etc. They also submit sediment/soil, sludge, fish, filters, paint and other samples. They collect some samples on a routine basis for monitoring purposes. In other cases, they respond to complaints, spills, fish kills or other crises.

The MPCA submits most of the high priority and Chain-of-Custody samples that we receive. They also submit most of our sediment/soil, fish, sludge and paint samples.

Shipping Protocol:
Most MPCA samples are transported/shipped on ice, in coolers because they are supposed to be maintained at a temperature of 4 degrees Celsius or less. The temperature needs to be checked and noted when the samples arrive.

Program Codes:
The MPCA uses over 50 different MDH Program Codes. There are a few that are used for routine samples, but many that are specialized. It is nearly impossible for us to determine the correct code if it is not provided by the collector. The routine codes are as follows:

PC MPCA-23 EOD-Lake Monitoring
PG MPCA-27 EOD-Routines
QW MPCA Closed Landfill Assessment

MPCA SAMPLE PROCESSING PROCEDURE

The MPCA courier delivers most of the samples we receive from them. Samples may be delivered by other courier services depending on where they are coming from.

Open coolers and boxes carefully. You may need to use a retractable blade "Exacto" knife to cut through the sealing tape. It is advisable to wear safety glasses while using a knife. Make sure that data sheets were included with the samples. Collectors usually put data sheets in plastic bags to protect them from moisture and they sometimes tape the bag to the lid of the cooler. If there are no data sheets (a very rare occurrence), refer to the return address to help you track down the collector. At the very least, you would then be able to contact the MPCA office that the samples were shipped from.

RECEIVING SAMPLES AND DATA SHEETS VIA IN-PERSON DELIVERY

When the MPCA courier (Ed Norwig) delivers samples, he will arrange them in order, on the counter. He never delivers samples without data sheets.

When other MPCA collectors bring in their samples, ask them to arrange them in order, on the counter. Make sure they filled out their data sheets completely and correctly. Do not allow

them to leave until the data sheet is complete and you have had a chance to compare the sample containers to the data sheets. In other words, go through steps 4,5,6,7, & 8 before the collector leaves.

CHECKING THE TEMPERATURE OF SAMPLES UPON ARRIVAL:

We normally check the sample temperature by using a temperature blank bottle that is kept in the cooler with the samples (see background information). It is most important to record the temperature information for bacteriology, BOD and Organic samples, but we should record it for all types of samples.

The MPCA courier takes and records the temperature for the samples he brings in and most other MPCA collectors do this for their own samples as well.

If there is no temperature blank, use a general bottle (be sure to clean the thermometer thoroughly first).
If there is no general bottle, you may use water that has pooled in the bottom of the cooler.
If there is no pooled water, but the samples are on ice or freezer packs, record the comment "no temperature blank, but samples on ice" on the data sheet.
If the samples are not on ice, record the comment "no temperature blank, samples not on ice".
If there is ice IN a sample, also make note of this.

CHECKING DATA SHEETS AND COMPARING THEM TO THE SAMPLE CONTAINERS:

Make sure there is a Program (Billing) Code on the Data Sheet. We cannot enter any information in the computer without a program code. If there is no code, contact the collector or the "report to" person listed on the data sheet. If you are unable to obtain the information before the samples must be submitted for testing, choose the code that seems most appropriate. Refer to the Chemistry Lab Handbook (and background information in this section) to aid you. The code can be changed once you obtain the correct information.

Make sure the station numbers, field numbers, sampling points and site ID's on the forms correspond with the information on the samples.

Compare the collection time on the bottle with the time listed on the data sheet. If there is a discrepancy, make note of it on the data sheet.

Compare the analysis codes requested with the bottles submitted. See step 6 for more detail on this.

DETERMINING THAT CORRECT BOTTLES WERE SUBMITTED FOR THE REQUESTED TESTS

Check the Analysis codes requested to be sure that all of the correct bottles have been submitted.

Refer to the bottle-type charts to make your determinations.

If you determine that the wrong bottles have been submitted, some substitutions can be made:
Thiosulfate Bacteriology bottles can be used for fluoride and nitrite, but not for nitrate or sulfate.
Non-thiosulfate Bacteriology bottles can be used for fluoride, nitrate, nitrite and sulfate.
General bottles can be used for nitrate, if sample is 2 days old or less.
Nutrient bottles can be used for nitrate (this is routinely done by the MPCA).
Free Cyanide and Total Cyanide bottles are interchangeable if there is adequate sample volume.
Other substitutions may be possible, check with the lab when incorrect bottles have been submitted.
In all cases above, check with the laboratory before submitting the sample and record a receiving comment that briefly describes the bottle substitution.

Bacteriology samples must be submitted in a sterile bottle, preferably our own Colilert, Thiosulfate or Non-Thiosulfate bottles. Occasionally, a collector may submit a bacteriology sample in their own sterile bottle, and this is usually acceptable, but check with the laboratory before submitting.

MPCA collectors rarely request code 327. The bacteriology codes they most commonly request are 310: fecal coliform and 311: fecal strep.

If the bottle submission problem cannot be resolved:
Notify the collector or "report to" person via phone or email. List the analyses that cannot be run and why.
If some of the analyses can still be run, cross out the codes that will not be run. Make note of the cancelled analyses and the date the collector was notified on the data sheet.

MPCA SAMPLE SIGN-IN PROCEDURE (SEE EXAMPLE OF DATA SHEET):

Most MPCA Data Sheets must be signed like a chain-of-custody form, even when the samples are not officially chain-of-custody. They use the following forms:
Standard MPCA form for water
Standard MPCA form for sediment
MPCA chain-of-custody form
MDH chain-of-custody form
MDH Organics Data Sheet
Forms from MPCA sub-contractors
The most common sub-contractors are Interpoll Labs, Conestoga-Rover and Foth & Van Dyke (the facilities that collect closed landfill samples).

The two standard MPCA forms are signed on the back of the white copy of the form. This is not strictly enforced, but if the collector or courier signs the form, then we should as well. The lab received date should also be recorded in the space provided on the front of the form, upper right.

The other forms are signed on the front of the top copy so that the information goes through all copies.

For all types of forms, the collector or courier will sign their name in the "relinquished by" column. They will also record the date and time of sample delivery.

A Sample Receiving employee must sign their name in the "received by" column, then record the date and time of sample acceptance.

MPCA SAMPLE SCHEDULING

Some MPCA collectors send us samples on a routine basis while others send samples more sporadically. They are all supposed to inform us of any BOD, CBOD, Fecal Coliform, Fecal Strep, and Ortho Phosphorus samples they will be submitting. The most important samples to know when they are coming are the Fecal Coliform samples since they only have a 24 hour hold time. They should also inform us of any other unusual samples they will bring in, such as Chain of Custody or Priority One samples. They may notify us by phone, email or fax.

If a collector calls, ask them for the following information:
Collector Name
Date and time samples will arrive at MDH
Total number of samples
Analyses requested on each sample
Sample type (lake water, stream water, sediment, paint, etc)
Priority One/Chain of Custody Information

If they do not provide enough information in an email, fax or phone message, contact them for more detail.

Pass this information onto the lab by sending a "New Task" through GroupWise to the bactichem unit. Be sure and mark the correct day of delivery in the message.

Sandy Bissonette and Beth Endersbe of the MPCA collect water samples on a routine basis from the spring through the fall of each year. They provide us with their planned schedule ahead of time, usually via email. They frequently order BOD and Fecal Coliform tests. They collect these samples from six different routes (or loops).

MPCA SAMPLE BOTTLE ORDERS

MPCA Warehouse Bottle Supply
The MPCA stocks their warehouse with MDH bacteriology, cyanide, metals, mercury, nutrient

and general (all 3 sizes) bottles. They fill most of their bottle orders from that supply. The MPCA courier (Ed Norwig) drops off and picks up bottle orders when he brings samples in.

Standing (Monthly) Bottle Orders
Periodically, Sandy Bissonette and Beth Endersbe send us their "standing" bottle order. Generally, Lab Services Shipping personnel fill these orders on a monthly basis. The MPCA courier picks up the orders and delivers them to the MPCA warehouse.

Specialized Bottle Orders
Local MPCA collectors frequently place more complicated and specialized bottle orders directly with us. Many of these orders are for emergencies and we try to fill them as needed. Most organic bottle orders are placed this way. If you are unsure what type of bottle the collector needs, refer them to the appropriate Unit Leader or other laboratory personnel for assistance.

Out-state Bottle Orders
Occasionally, out-state MPCA collectors place orders that they want shipped directly to them and we try to accommodate them. However, it the order is for a large number of routine bottles (general, nutrient, metal, cyanide, bacteriology etc), refer them to Ed Norwig in the MPCA warehouse.

MPCA CLOSED LANDFILL PROGRAM

The Minnesota Pollution Control Agency (MPCA) administers this program in order to monitor the groundwater quality of sanitary landfills that are no longer in active use. The MPCA subcontracts with various private labs to collect the samples and deliver them to MDH for testing. We also provide sample bottles for these collectors.

We have standing (routine) bottle orders set up for some of the landfills that have a regular sampling schedule. The order information is in a yellow folder that is stored in a rack on the counter.

The parameter (test code) lists for these standing orders are in the desk file drawer, each in their own labeled folder. The parameter lists should be brought with the lab sheet every time.

Interpoll Labs faxes their bottle orders to us as needed. Their bottle orders list the parameters that will be run on the samples and we must determine the necessary bottles from this list. The parameter list is in alphabetical order, rather than by bottle type or numerical order. This makes it difficult to figure out the type of bottles needed when a person is new to sample receiving. Listed on the next page are the codes in the parameter list order with the bottle type listed by each code. A list of codes in numerical order follows, and finally a list of codes taken from each bottle type are listed.

Alphabetical List	Test Code	Bottle type
Alkalinity	22	General 1 liter
Ammonia Nitrogen	64	Nutrient
Arsenic	108/109	Metals
Barium	113/114	Metals
BOD (bacti oxygen demand)	96	General 2 liter
Bromide (rarely ordered)	455	two 40 ml vials (ask organics)
Cadmium	122/123	Metals
Calcium	694/695	Metals
CBOD	83	General 2 liter
Chloride	23	General 1liter
Chromium	129/130	Metals
Cobalt	136/137	Metals
Copper	145/146	Metals
Iron	152/154	Metals
Lead	157/158	Metals
Magnesium	696/697	Metals
Manganese	166/168	Metals
Mercury	200/202	Mercury
Nickel	171/172	Metals
Nitrate (nitrate/nitrite)	69	Nutrient
Nitrite	67	General 1 liter

Nitrogen (Ammonia)	64	Nutrient
Potassium	255/256	Metals
Sodium	257/258	Metals
Solids, total dissolved	5	General 1 liter
Solids, total suspended	3	General 1 liter
Sulfate	28	General 1 liter
Volatile Organic Compounds	498	40 ml VOC vials
Vanadium	248/249	Metals
Zinc	194/195	Metals

*Special dissolved analyses: Some of the metal and mercury samples will be filtered in the field. Make sure that you make note of which ones are filtered on the paperwork. The paperwork should be noted, but many times the paperwork is incorrect and it needs to be checked. When entering the analytical codes, make sure dissolved codes are entered in for the samples that were filtered. The parameter lists might not indicate what the dissolved codes are, so they will have to be look up in the Environmental Laboratory Handbook. This tends to take up a lot of time, so if there are any other samples that need to be delivered to the labs, do that before working on the Interpoll samples.

Numerical List

Analysis	**Test Code**	**Bottle Type**
Solids, total suspended	3	General 1 liter
Solids, total dissolved	5	General 1 liter
Alkalinity	22	General 1 liter
Chloride	23	General 1 liter
Sulfate	28	General 1 liter
Phosphate (dissolved)*	60	Nutrient
Nitrogen (Ammonia)	64	Nutrient
Nitrite (total)	67	General 1 liter
Nitrate (total)	69	Nutrient
Nitrite (dissolved)*	73	General 125 ml
Nitrate (dissolved)*	78	Nutrient
CBOD	83	General 2 liter
BOD	96	General 2 liter
Arsenic	108/109	Metals
Barium	113/114	Metals
Cadmium	122/123	Metals
Chromium	129/130	Metals
Cobalt	136/137	Metals
Copper	145/146	Metals
Iron	152/154	Metals

Lead	157/158	Metals
Manganese	166/168	Metals
Nickel	171/172	Metals
Zinc	194/195	Metals
Mercury	200/202	Mercury
Vanadium	248/249	Metals
Potassium	255/256	Metals
Sodium	257/258	Metals
Calcium	694/695	Metals
Magnesium	696/697	Metals
Bromide (rarely ordered)	455	2 - 40 ml vials (ask organics)
VOC's	498	3 VOC vials/set

Parameter List by Bottle Type:

General 1 liter: 3, 5, 22, 23, 28, 67

General 125 ml: 73

General 2 liter: 83, 96

Metals: 108, 109, 113, 114, 122, 123, 129, 130, 136, 137, 145, 146, 152, 154, 157, 158, 166, 168, 171, 172, 194, 195, 248, 249, 255, 256, 257, 258, 694, 695, 696, 697

Mercury: 200, 202

Nutrient: 60, 64, 69, 78

VOC Vials: 498, 462 (3 vials for each code)

Tests not run at MDH: Sometimes there are parameters on the list that are not run at MDH but are analyzed by the collectors in the field. They are not assigned test codes on the parameter list (or by us).
These analyses are as follows:
Eh (mV), Iron II, Methane and Sulfide. Note that when Iron II is field analyzed, our lab must run Iron (codes 152/154). This may not be marked on the parameter list.

Cation-Anion Balance, Code 996: If this code is on a parameter list, do not enter it in the computer. It is a calculation that is done automatically when certain other tests are ordered.

Anoka Landfill Wetlands Samples: These are collected on a monthly basis, but Interpoll always faxes the order when needed; it is not a standing order done on a specific day. The order includes the parameter (analysis code) list. You can recognize the order by the sampling points: Cascade, Lift Station, Sed Basin, Splitter Tank, Manhole (MH)- 1AB, -2AB, -3AB, -4AB and MH-1BC, -2BC, -3BC, -4BC. This is a total of 12 sites, and they will need one set of VOC trip blanks.

BOD (code 96) and TSS (code 3) are run on these samples, so we give them 2 liter General bottles. We also provide Nutrient bottles and VOC vials for routine tests.

Therefore, the bottle order for this site is as follows:

12 Two liter General bottles
12 Metals bottles
12 Mercury bottles
12 Nutrient bottles
12 sets of VOC vials
1 set of VOC Trip Blanks

MPCA- BAYWEST

Meth Samples:
The samples from Baywest are usually Meth samples. The normal numbering procedure is still used. The program code for these samples is LG. The analysis code should be 484, which is the drug analysis code.

The distribution of the paperwork is however different. The paperwork is one of the three-page Chain of Custody forms. The pink copy goes to the collector. The yellow copy will be the one sent to Clerical. The white copy will be sent with the samples upstairs to the Organics Lab. They will keep a log book of the forms.

DRO Samples:
Baywest will bring in DRO samples for the Reserve Mining Project from time to time. Do not change the program code to LG. The pH of these samples will have to be checked and recorded on the pH verification sheet. A copy of this sheet will go with the samples and another one will go to Bill Scruton. The pH will have to be less than 2, so you might have to adjust as needed. When entering in the samples, a comment must be made for samples that are to be used for Matrix Spikes (MS) or Duplicate (MSD). This helps to notify the laboratory personnel that they have to do some spikes. Also put an orange dot with MS or MSD on the bottle. Deliver the samples to the Organics Laboratory with copies of the paperwork.

MINNESOTA OSHA (LABOR AND INDUSTRY) SAMPLES

Minnesota OSHA is part of the State Labor and Industry Agency. They collect investigative samples from worksites as part of their response to complaints.

OSHA very rarely submits any water samples. Instead they submit:
Bulk samples for Metals and Asbestos
Carbon Air filters for solvents
Cartridge filters for formaldehyde
Cassette filters for Metals and Silica
Dust samples for Metals
Paint samples for Metals
Wipe samples for Metals
Other Miscellaneous samples.

THE PROGRAM CODE FOR ALL MN/OSHA SAMPLES IS MG.

The Data Sheet used for MN/OSHA samples does not have analysis code columns, nor does it have the Program Code printed anywhere. This makes it more difficult to process the samples because we have to look up the analysis codes for each set of samples that come in.

One section of the form has a list of Analytical Methods that looks like this:

Metals AAFL AAFU ICP
Solvents GC GC/MS HPLC
Asbestos Ph.C PLM TEM
Silica X-ray
Misc.

Analysts are supposed to circle the method they want and we use the information to help determine which analytical codes to assign and which Lab Unit should receive the samples.
Sometimes they write their analysis requests on the bottom of the form instead.
Solvent samples are for the Organics Lab.
Bactichem and Radiation rarely receive OSHA samples.

Metals: The Periodic Table of Elements Chemical Symbol of each Metal is listed after the name because OSHA collectors often request metals tests this way.

Metals Analysis Codes:

653	Aluminum	Al
654	Antimony	Sb
655	Arsenic	As
656	Barium	Ba
657	Beryllium	Be

Metals Digest/Prep Codes:

682	Miscellaneous
683	Filters
684	Wipes
685	Bulks
686	Dust

658	Boron	B
659	Cadmium	Cd
660	Calcium	Ca
661	Chromium	Cr
662	Chromium, Hexavalent	Cr-6
663	Cobalt	Co
664	Copper	Cu
665	Iron	Fe
666	Lead	Pb
667	Magnesium	Mg
668	Manganese	Mn
669	Mercury	Hg
670	Molybdenum	Mo
671	Nickel	Ni
672	Potassium	K
673	Selenium	Se
674	Silver	Ag
675	Sodium	Na
676	Thallium	Tl
677	Tin	Sn
678	Titanium	Ti
679	Vanadium	V
680	Zinc	Zn
688	Bismuth	Bi

981 Formaldehyde, Cartridge: These samples must be sent to a private lab. They should be delivered to the metals unit.

687 Paint

One Digest/Prep Code must be assigned to each OSHA Metals sample along with the Analysis Codes.

If Metals Group 1 is requested, it consists of the following codes:

661 Chromium (+Insol. Salts)
664 Copper (fume, as Cu)
665 Iron (oxide fume)
668 Manganese (fume as Mn)
671 Nickel (+Insol. Comp.)
680 Zinc (oxide fume)

Organics Code:

597 Solvents (Air)

This code is assigned to all OSHA Organics samples. The following is a partial list of solvents that fall under this code:

Epichlorohydrin
Ethanol
Ethyl Benzene
Heptanon
Isobutyl Alcohol
Methylene Chloride
Petroleum Distillates
Stoddard Solvents
Toluene
Xylenes

We do not analyze for formaldehyde as a solvent but the Metals unit can run a different type of analysis for it. See metals codes on previous page.

Misc. Samples:
If there are no codes for the wanted tests (ex. Ozone) contact the assistant lab manager to set up subcontracting them to a different laboratory.

MINNESOTA OSHA SAMPLE PROCESSING PROCEDURE:
LABELING OSHA SAMPLES:

Do not remove the samples from their bags (the labs will do this).
Just clip the labels and paperwork to the bag containing the samples. The laboratory personnel will deal with labeling themselves.

MAKE A COPY OF THE DATA SHEET:

The copy is for the clerical unit.
Attach the original to the bag/labels.
The Metals Department wants the copy of the sheet to be delivered to them and the original to be sent to the Clerical Unit.

MISCELLANEOUS SAMPLES
PRIVATE WELL WATER TESTING

The only analysis that we do for private homeowners on a routine basis is the testing of new homeowner-drilled wells through the New Well Program. These samples should be accompanied by the appropriate paperwork.

We also test flooded well samples when there has been flooding in a given area of the state. In this case, we will be notified ahead of time that the Flooded Well Program has been activated and we should expect samples. These samples should also be accompanied by the appropriate paperwork.

All other private well testing must be pre-arranged through the Well Management program. In most cases, the homeowner will be directed to a local or county program for their testing needs.

Direct any inquiries to:

Well Management at 651-201- 4600 OR
Francine Lafayette at 651-201-4592

Appendix C

MDH Environmental Laboratory Standard Operating Procedures

QuikChem® Method 10-107-04-3-D

DETERMINATION OF TOTAL NITROGEN IN WATERS BY IN-LINE DIGESTION FOLLOWED BY FLOW INJECTION ANALYSIS

- IMIDAZOLE BUFFER METHOD -

0.05 to 5.0 mg N/L Low Range
0.2 to 20.0 mg N/L High Range

(Method also includes Manifold Alterations to Analyze Nitrate/Nitrite)

Written by Scott Tucker

Applications Group

Revision Date:

2 December 2010

LACHAT INSTRUMENTS
5600 LINDBURGH DRIVE
LOVELAND, CO 80539 USA

LACHAT INSTRUMENTS
A Hach Company Brand

QuikChem® Method 10-107-04-3-D

Total Nitrogen, In-line Persulfate Digestion

-Imidazole Buffer Method –

(Method also includes Manifold Alterations to Analyze Nitrate/Nitrite, see section 17.5)

0.05 to 5.0 mg N/L
0.2 to 20.0 mg N/L

– Principle –

Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

– Interferences –

1. Chloride is a suspected interference. Seawater, when spiked at 5 mg N/L as ammonia, gave < 5% recovery.

– Special Apparatus –

Please see Parts and Price list for Ordering Information

1. Lachat Sample Preparation Module, A30X11 (X=1 for 110V, x=2 for 220V) with UV-254 lamp.
2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

CONTENTS

QuikChem® Method 10-107-04-3-D

DETERMINATION OF TOTAL NITROGEN BY IN-LINE DIGESTION BY FLOW INJECTION ANALYSIS COLORIMETRY

1. SCOPE AND APPLICATION

1.1. Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

1.2. Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

1.3. After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

1.4. The method will recover nearly all forms of nitrogen. Nitrate and nitrite are recovered in this method. They are not recovered in the conventional Kjeldahl nitrogen method. Thus the resultant concentration for this method is termed total nitrogen and not Kjeldahl nitrogen.

1.5. The applicable range is 0.05 to 5.0 mg N/L for the low range and 0.2 to 20.0 mg N/L for the high range. The method detection limit is 0.003 mg N/L for the low range and 0.008 mg N/L for the high range. The method throughput is 45 injections per hour.

2. SUMMARY OF METHOD

2.1. Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

2.2. Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

2.3. After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a

diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

3. DEFINITIONS

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.1. ANALYTICAL BATCH -- The set of samples extracted/distilled/or digested at the same time to a maximum of 10 samples.

3.2. CALIBRATION BLANK (CB) -- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

3.3. CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4. FIELD BLANK (FMB) -- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.5. FIELD DUPLICATE (FD) -- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.6. LABORATORY BLANK (LRB) -- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7. LABORATORY CONTROL STANDARD (LCS) -- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

3.8. LABORATORY DUPLICATE (LD) -- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

3.9. QUALITY CONTROL CHECK SAMPLE (QCS) -- A sample containing analytes of interest at known concentrations (true values) of analytes. The QCS is obtained for a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

3.10. METHOD DETECTION LIMIT (MDL) -- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

4. INTERFERENCES

4.1. Chloride is a suspected interference.

5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

5.3.1. Cadmium

5.3.2. Sulfuric Acid

5.3.3. Phosphoric acid

5.3.4. Potassium persulfate

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1. Sampler

6.3.2. Multichannel proportioning pump

6.3.3. Reaction unit or manifold

6.3.4. Colorimetric detector

6.3.5. Data system

6.4. Special Apparatus

6.4.1. Lachat Sample Preparation Module, A30X11 (X=1 for 110V, x=2 for 220V) with UV-254 lamp.

6.4.2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

7. REAGENTS AND STANDARDS

7.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

Degassing with helium: 5 min?

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Imidazole Buffer, pH ~ 7.4

By Volume: In a **1L** volumetric flask, add ~ **600 ml** of **DI water**, **6.8 g** of **Imidazole** ($C_3H_4N_2$), and **2 ml** of **concentrated HCl** (it is recommended that addition of the HCl be carried out in a hood). Swirl to dissolve the imidazole and dilute to 1 L with DI water. The imidazole buffer was shown to be stable for at least one month.

Reagent 2. Sulfanilamide Color Reagent

By Volume: To a **1 L** volumetric flask add about **600 mL DI water**. Then add **100 mL 85% phosphoric acid** (H_3PO_4), **40.0 g sulfanilamide and 1.0 g N-(1-naphthyl)-ethylenediamine dihydrochloride** (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark with **DI water** and invert to mix. Store in a dark bottle and discard when the solution turns pink.

By Weight: To a tared, dark **1 L** container add **876 g DI water, 170 g 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake until wetted and stir with a stir bar for 30 minutes until dissolved. Store in a dark bottle and discard when the solution turns pink.

Reagent 3. Potassium Persulfate Oxidant

43 of $Na_2S_2O_8$

By Volume: In a **1 L** volumetric flask containing approximately **900 mL water,** ~~add 49 g potassium persulfate~~ ($K_2S_2O_8$). Add **10 g disodium tetraborate decahydrate** ~~($Na_2B_4O_7 \cdot 10H_2O$).~~ Add a magnetic stir bar, dissolve and dilute to the mark with **DI water**. Invert to mix. Gentle heating or a warm water bath is required for complete dissolution.

potassium peroxodisulfate

By Weight: To a tared **1 L** container, add **975 g DI water** and **49 g potassium persulfate** ($K_2S_2O_8$). Add **10 g disodium tetraborate decahydrate** ($Na_2B_4O_7 \cdot 10H_2O$). Add a magnetic stir bar sir until dissolved. Gentle heating or a warm water bath is required for complete dissolution.

Potassium persulfate is known to have nitrogen contamination. There are two suggestions to reduce this contamination 1) re-crystallize the potassium persulfate, or 2) use sodium persulfate. If you choose to use sodium persulfate, use **43 g** of **$Na_2S_2O_8$** instead ~~of 49 g of $K_2S_2O_8$~~.

Potassium persulfate re-crystallization procedure:

1. Dissolve 100 g of potassium persulfate in approximately 600 ml of Milli-Q previously heated to 60° C. Use a medium sized stir bar and a 1000 mL flask.

2. Filter the solution rapidly through a sintered glass funnel.

3. Rinse the 1000 mL flask.

4. Poor filtrate back into the flask used to heat the potassium persulfate solution.

5. Cool solution to about 4° C by placing the flask in ice water. Whirl the flask continuously to prevent the solution from freezing.

6. Filter the 4° C solution and wash with 1 or 2 squeezes of ice cold Milli-Q, save the white solid.

7. Discard the filtrate from the sidearm flask.

8. Rinse the flask used to cool the solution with Milli-Q

9. Fill the flask with 450ml of Milli-Q and heat to 60° C.

10. Add the crystals from step 5 and mix into solution.

11. Repeat steps 4 and 5. The white granules on top of the filter are crystals!

12. Dry crystals in vacuo over anhydrous calcium chloride. Rapid drying in a good vacuum and thus at a low temperature is essential as this will minimize the sulfuric acid formation on the crystals.

The yield is about 80%. The effect is illustrated by the blank obtained in the standard procedure-0.178 for the original reagent, 0.02 after one re-crystallization and 0.01 µmole of N after two re-crystallizations.

Reagent 4. Buffer Solution for Digestion

By Volume: In a **1 L** volumetric flask dissolve **25.0 g disodium tetraborate decahydrate** ($Na_2B_4O_7 \cdot 10\ H_2O$) and **3.0 g sodium hydroxide** (NaOH) in approximately **900 mL water.** Adjust to pH = 9.0 with sodium hydroxide or hydrochloric acid. Add a magnetic stirbar, dissolve and dilute to the mark with **DI water**. Gentle heating may be required for complete dissolution. Invert to mix.

7.2. PREPARATION OF STANDARDS

To prepare the stock and working standards, the following containers will be required:

By Volume: Two 1 L volumetric flasks and seven 250 mL volumetric flasks.

By Weight: Two 1 L containers and seven 250 mL containers.

Standard 1. Stock Standard 1000 mg N/L

In a **1 L volumetric flask** dissolve **7.221 g potassium nitrate** (KNO_3), pre-dried (60°C for 1 hour) or **4.93 g sodium nitrite** ($NaNO_2$) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. When refrigerated the nitrate standard may be stored for up to three months. Standards prepared as nitrate are more stable than those prepared as nitrite.

Standard 2. 100.0 mg N/L

By Volume: In a **1 L** volumetric flask add **100 mL of Standard 1** (1000 mg N/L). Dilute to the mark with **DI water** invert to mix. Prepare fresh weekly.

Standard 3. 10.0 mg N/L

By Volume: In a **1 L** volumetric flask add **10 mL of Standard 1** (1000 mg N/L). Dilute to the mark with **DI water** invert to mix. Prepare fresh weekly.

Low Range Standards

Working Standards (Prepare Daily) Concentration mg N/L	**A** 5.00	**B** 2.00	**C** 1.00	**D** 0.40	**E** 0.20	**F** 0.10	**G** 0.05	**H** 0.00

By Volume

Volume (mL) of **standard 3** diluted to 250 mL with DI water.	125	50	25	10	5	2.5	1.25	0

By Weight

Weight (g) of **standard 3** diluted to final weight (~250 g) divide by **factor** below with DI water.	125	50	25	10	5	2.5	1.25	---
Division Factor Divide exact weight of the standard by this **factor** to give final weight.	0.50	0.20	0.10	0.04	0.02	0.01	0.005	---

High Range Standards

Working Standards (Prepare Daily) Concentration mg N/L	**B** 20.0	**C** 10.0	**D** 5.00	**E** 2.00	**F** 1.00	**G** 0.40	**H** 0.20	**I** 0.00

By Volume

Volume (mL) of **standard 2** diluted to 250 mL with DI water.	50	---	---	---	---	---	---	---
Volume (mL) of **standard 3** diluted to 250 mL with DI water.	---	250	125	50	25	10.0	5.0	0

By Weight

Weight (g) of **standard 2** diluted to final weight (~250 g) divide by **factor** below with DI water.	50	---	---	---	---	---	---	---
Weight (g) of **standard 3** diluted to final weight (~250 g) divide by **factor** below with DI water.	50	250	125	50	25	10.0	5.0	0
Division Factor Divide exact weight of the standard by this **factor** to give final weight.	0.20	---	0.50	0.20	0.10	0.04	0.02	---

Stock Digestion Check Standards: 1000 mg N/L

In a **500 mL volumetric flask** dissolve **x.xx g** test compound (see table) in about **400 mL DI water**. Dilute to the mark with **DI water** and invert to mix.

Stock stds	Compound	g/500ml	Formula	FW
1	Ammonium p-toluenesulfonate	6.755	$C_7H_{11}O_3SN$	189.2
2	Nicotinic acid p-toluenesulfonate	10.542	$C_{13}H_{13}O_5SN$	295.3
3	Ammonium sulfate	2.359	$(NH_4)_2SO_4$	132.1
4	Urea	1.072	H_2NCONH_2	60.1
5	Disodium EDTA, dihydrate	6.644	$NaO_2CCH_2N(CH_2CO_2H)$ $CH_2CH_2N(CH_2CO_2Na)$ $CH_2CO_2H_2H_2O$	372.2

Working Digestion Check Standards (1 - 5) 5 mg N/L

By Volume: In a **500 ml** volumetric flask add **2.5 mL of Stock Digestion Check Standard # (1, 2, 3, 4, or 5** (1000 mg N/L). Dilute to the mark with **DI water** invert to mix. Prepare fresh weekly.

Working Standards (1-5)	**A**
Concentration mg N/L	5.00

By Volume

Volume (mL) of **check standard (1, 2...or 5)** diluted to 250 mL with DI water	2.5

By Weight

Weight (g) of **check standard (1, 2...or 5)** diluted to final weight (~250 g) divide by **factor** below with DI Water	2.5
Division Factor Divide exact weight of the standard by this **factor** to give final weight	0.005

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (maximum of 2 mL concentrated H_2SO_4 per liter) and refrigerated. **CAUTION:** Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

8.2. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

9. QUALITY CONTROL

9.1. Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.1.1. Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in section 9.3.

9.1.2. Analyses of laboratory blanks are required to demonstrate freedom from contamination.

9.1.3. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.4. The laboratory should maintain records to define the quality of data that is generated.

9.2. INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1. Method Detection Limit (MDL) --To establish the ability to detect the analyte, the analyst shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in section 1.2 must be achieved prior to the practice of this method.

9.2.2. Initial Precision and Recovery -- To establish the ability to generate acceptable precision results, the operator shall perform 10 replicates of a mid-range standard, according to the procedure beginning in Section 11.

9.2.2.1. Using the results of the replicates compute the average percent recovery (X) and the standard deviation (s) for the analyte. Use the following equation for the calculation of the standard deviation.

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

Where, n = Number of samples, x = concentration in each sample

9.2.2.2. Compare s and x results with the corresponding data in Section 17. If the results meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If however, s and x do not match the data in Section 17, system performance is unacceptable. In this event correct the problem, and repeat the test.

9.3. Matrix spikes- The laboratory must spike, in duplicate, a minimum of 10 percent of all samples (one sample in each batch of ten samples) from a given sampling site or if for compliance monitoring, from a given discharge. The two sample aliquots shall be spiked with the stock standard (section 7.2).

9.3.1. The concentration of the spike in the sample shall be determined as follows:

9.3.1.1. If, as in compliance monitoring, the concentration of the analyte in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), which ever is higher.

9.3.1.2. If the concentration of the analyte in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard used in Section 9.2.5 or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2. Analyze one sample aliquot out of each set of ten samples from each site or discharge according to the procedure beginning in Section 11 to determine the background concentration of (B) of the analyte.

9.3.2.1. If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2. Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A)

9.3.3. Calculate the percent recovery (P) of the analyte in each aliquot using the following equation.

$$P = \frac{(A - B)100}{T}$$

Where, A = Measured concentration of analyte after spiking, B = measured background concentration of analyte, T = True concentration of the spike

9.3.4. The percent recovery of the analyte should meet current laboratory acceptance criteria.

9.3.4.1. If the results of the spike fail the acceptance criteria and the recovery of the QC standard in the ongoing precision and recovery test of the analytical batch is within the current laboratory acceptance criteria, an interference is present. In this case, the results may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method, repeat the test required in Section 9.1.2 and repeat the analysis of the sample and the matrix spike.

9.3.4.2. If the results of both the spike and ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample reanalyzed.

9.3.5. Compute the relative percent difference (RPD) between two sample results using the following equation:

$$RPD = \frac{(D_1 - D_2)}{(D_1 + D_2)/2} \times 100$$

Where, D1 = Concentration of analyte in the sample, D2 = Concentration of analyte in the second (duplicate) sample.

9.3.6. The RPD for duplicates shall meet the current laboratory acceptance criteria. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

9.4. Laboratory blanks - Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1. Analyze a laboratory reagent water blank initially (with the test in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2. If analyte is detected in the blank at a concentration greater than MDL (Section 3.10.), analysis of the samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.5. Calibration Verification Verify calibration using the procedure described in Section 10

9.6. On-going Precision and Recovery (OPR) - With every analytical batch, a midrange standard must be prepared using the procedure described in Section 11.

9.6.1. Compare the results with the current laboratory acceptance criteria. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

9.7. Quality Control Samples (QCS) It is suggested that the laboratory obtain and/or prepare a quality control sample using a source different from the source routinely used in Section 7. The QCS is used to verify the concentrations of the calibration standards.

9.8. Depending on the specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10. CALIBRATION AND STANDARDIZATION

10.1. Prepare reagents and standards as described in Section 7.

10.2. Set up manifold as shown in Section 17.

10.3. Input data system parameters as shown in Section 17.

10.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

10.5. Place standards in the sampler. Input the information required by the data system.

10.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the peak area for each standard to determine the calibration curve.

10.7. Verify calibration using a midrange calibration standard every ten samples or every analytical batch. Compute the percent recovery using the following equation:

$$\%recovery = \frac{D}{K} \times 100$$

Where, D = Determined concentration of analyte in the calibration standard, K = Actual concentration of the analyte in the calibration standard

10.8. If % recovery exceeds +/-10%, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed

11. PROCEDURE

11.1. SAMPLE PRETREATMENT - PROCEDURE

11.1.1. Samples may be determined without preservation or preserved with sulfuric acid as directed above.

11.1.2. Both standards and samples should be carried through this procedure. If samples have been preserved with sulfuric acid, standards should be preserved in the same manner.

11.1.3. Samples may be homogenized in a device designed for this purpose. However, turbid samples should be filtered since the digestion effectiveness on nitrogen containing particles is unknown.

11.2. CALIBRATION PROCEDURE

11.2.1. Prepare reagent and standards as described in Section 7.

11.2.2. Set up manifold as shown in Section 17.

11.2.3. Input data system parameters as shown in Section 17.

11.2.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

11.2.5. Place samples and/or standards in the sampler. Input the information required by the data system, such as concentration, replicates and QuikChem scheme (See Section 17).

11.2.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

11.3. SYSTEM NOTES

11.3.1. For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual. This guide is also available on request from Lachat.

11.3.2. Allow more than 20 minutes for the heating unit in the sample prep module to warm to 105°C. Tubing crimp formation has been observed in the past with the PTFE manifold tubing when no liquid is running through heater tubing and the tubing is allowed to bake. Running liquid through the heater whenever the temperature is above 80°C is necessary.

11.3.3. Since the digestion occurs prior to injecting the sample and since there is an air segment between the sample and the sampler wash solution, the valve and sample timing parameters are critical. It is important to verify that the center of the sample zone is injected.

11.3.4. Because the blank peak in this method is due to nitrogen in the buffer and persulfate solid reagents, it is important to use the best purity available.

11.3.5. Digestion efficiency should be verified by determining non-nitrate standards at regular intervals. A good plan is to use urea and nicotinic acid. Urea recovery

goes down when the digestion is too rigorous and nicotinic acid requires optimal functioning of all digestion parameters for recovery >95%.

11.3.6 To prevent ammonium contamination during system start up and shut down, use a separate wash vessel dedicated to the ammonium chloride buffer.

11.3.7 It is advisable to periodically determine a nitrite standard to check column efficiency. If column efficiency is < 90% replace the column.

11.3.8 System Maintenance for best results:

11.3.8.1. Change PVC tubing every three days.

11.3.8.2. Change tubular membrane of debubbler every two days. (The membranes in the alternate debubbler are changed only as required, and may last 3-4 weeks or more).

11.3.8.3. Change cadmium column every 200 samples.

11.3.9 Check list before running real samples.

11.3.9.1. Check that the method's timing has been correctly set by running food dye (bypass cadmium column at this time).

11.3.9.2. Check the temperature of digestion module (105° for TN and 125° for TP)

11.3.9.3. Check that all reagents are prepared correctly, to ensure there is no precipitation in the digestion buffer solution.

11.3.9.4. Check that the debubbler is in good condition, and it is efficiently debubbling by running one duplicate standard. (Cadmium column should be in correct position for TN). Please note that there may condensation at the outlet of the alternate debubbler. A true leak occurs around the edge of the disc with this debubbler. 7.3.9.5. Check that the cadmium column is in good condition by looking at the color. The color of cadmium should be black or dark gray. If white precipitated material is seen in the column, replacement is necessary.

11.3.9.6. If acceptable, duplicate peaks are produced, real samples can be run. Otherwise adjust the timing and troubleshoot or perform maintainence on the system until it is in good condition.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

12.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in mg N/L.

13. METHOD PERFORMANCE

13.1. The method support data are presented in Section 11. This data was generated according to a Lachat Work Instruction during development of the method.

13.2. Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

14. POLLUTION PREVENTION

14.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the United States Environmental Agency (USEPA) recommends recycling as the next best option.

14.2. The quantity of chemicals purchased should be based on expected usage during their shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operation. Compliance with all sewage discharge permits and regulations is also required.

15.2. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

16. REFERENCES

16.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. EPA-600/R-93/100, Revised August 1993, Method 353.2.

16.2. Determination of Nitrogen in Water: Comparison of a Continuous-flow method with on-line UV Digestion with the original Kjeldahl method, Hennie Kroon, Analytica Chemica Acta, 276, (1993) 287-293.

16.3 Lachat Instruments Inc., QuikChem Method 10-107-04-3-P.

17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000/8500

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	40 samples/h, 90 s/sample
Pump Speed:	35
Cycle Period:	90

Analyte Data:

Concentration Units:	mg N/L
Peak Base Width:	42 s
Inject to Peak Start:	30.8 s
Chemistry:	Direct/Bipolar

Calibration Data:

Low Range

Level	1	2	3	4	5	6	7	8
Concentration mg N/L	5.00	2.00	1.00	0.40	0.20	0.10	0.05	0.00

High Range

Level	1	2	3	4	5	6	7	8
Concentration mg N/L	20.0	10.0	5.00	2.00	1.00	0.40	0.20	0.00

Calibration Rep Handling:	Average
Calibration Fit Type:	2nd Order Polynomial
Weighting Method:	1/x
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	19 s
Probe in Sample Period:	60 s

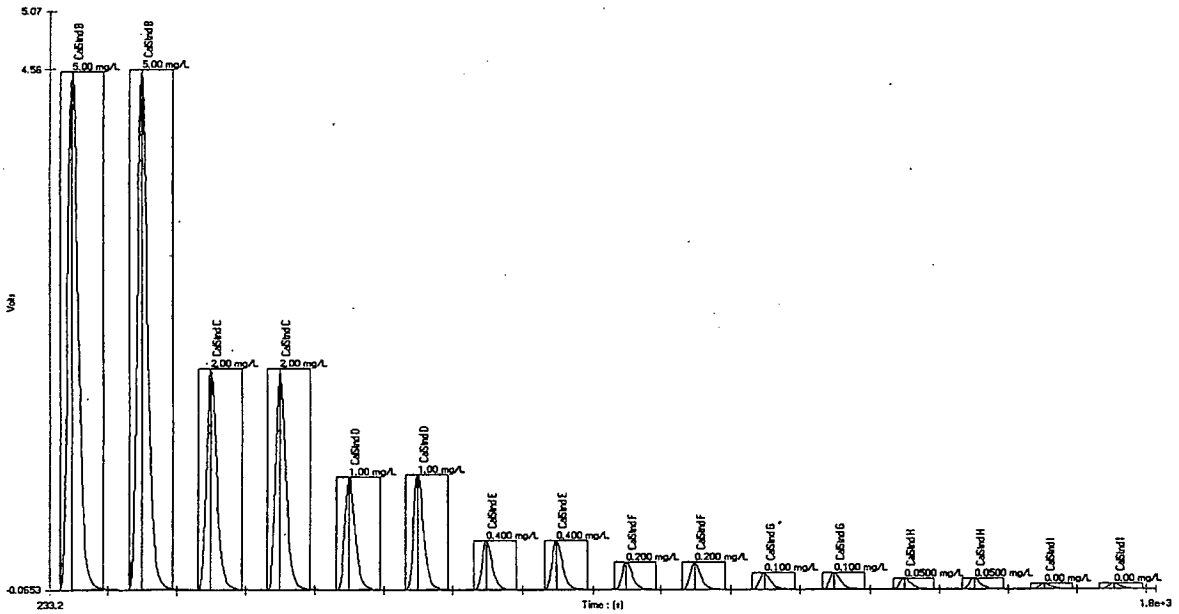
Valve Timing:

Load Period:	30 s
Inject Period:	60 s
Sample Reaches 1st Valve	160 s*

*The time it takes the sample to reach the valve needs to be timed for the specific manifold being utilized. The time listed is just a starting point. The best way to calculate the time to valve is as follows: When the sampler probe travels to the sample, it will draw up an air slug. Start timing when the sampler probe goes into the sample, then watch the air slug travel through the heater, then out of the UV lamp. Once it reaches the debubbler stop timing, and add 5 to 10 seconds for the beginning of the sample slug to reach the valve. This recorded time with the additional 5 to 10 seconds added will be the time that should be entered in the software as the sample reaches first valve.

17.2. SUPPORT DATA FOR QUIKCHEM 8000/8500

Calibration Data for Total Nitrogen Low Range



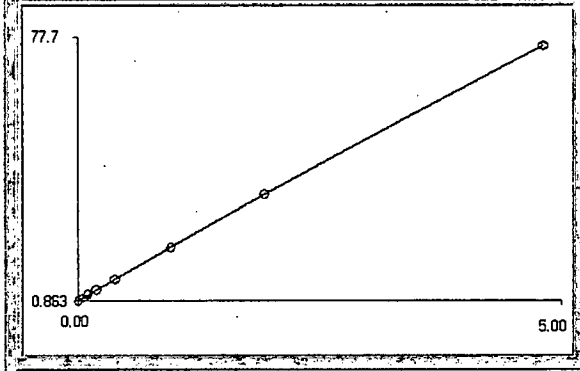
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

Calibration Graph and Statistics

Calibration Results - Channel 1

TN

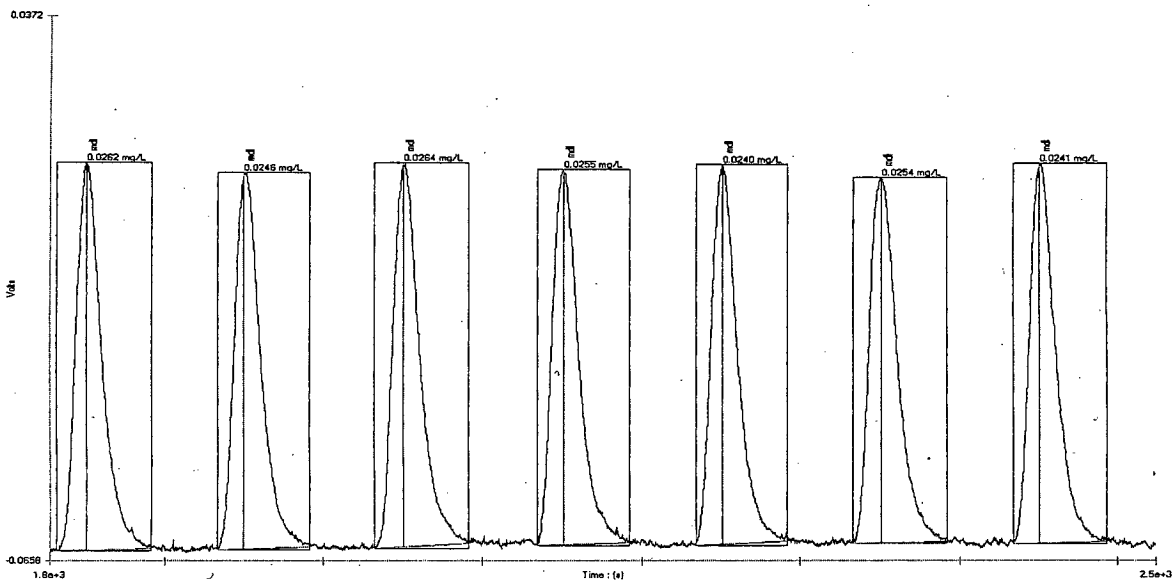
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	5.00	1	77.4	4.60	0.3	0.2	☐	4.99	11/19/2007	12:52:36 PM
2	5.00	2	77.7	4.62	0.3	-0.2	☐	5.01	11/19/2007	12:54:14 PM
3	2.00	1	32.9	1.98	0.3	-0.7	☐	2.01	11/19/2007	12:55:52 PM
4	2.00	2	32.8	1.97	0.3	-0.2	☐	2.01	11/19/2007	12:57:30 PM
5	1.00	1	16.9	1.01	0.6	0.8	☐	0.991	11/19/2007	12:59:08 PM
6	1.00	2	16.7	1.03	0.6	1.6	☐	0.982	11/19/2007	1:00:45 PM
7	0.400	1	7.44	0.441	0.4	-0.6	☐	0.402	11/19/2007	1:02:22 PM
8	0.400	2	7.40	0.437	0.4	0.0	☐	0.400	11/19/2007	1:04:03 PM
9	0.200	1	4.11	0.243	1.1	1.2	☐	0.197	11/19/2007	1:05:42 PM
10	0.200	2	4.18	0.244	1.1	-0.4	☐	0.201	11/19/2007	1:07:18 PM
11	0.100	1	2.59	0.147	0.3	-2.2	☐	0.103	11/19/2007	1:08:57 PM
12	0.100	2	2.58	0.147	0.3	-1.8	☐	0.103	11/19/2007	1:10:36 PM
13	0.0500	1	1.77	0.0970	1.3	-2.4	☐	0.0526	11/19/2007	1:12:13 PM
14	0.0500	2	1.74	0.0949	1.3	-0.6	☐	0.0507	11/19/2007	1:13:52 PM
15	0.00	1	0.863	0.0456			☐	-2.86e-3	11/19/2007	1:15:30 PM
16	0.00	2	0.874	0.0470			☐	-2.16e-3	11/19/2007	1:17:07 PM



Area = -0.190 * Conc^2 + 16.3 * Conc + 0.912
Conc = 5.13e-5 * Area^2 + 0.0612 * Area - 0.0557
Correlation Coefficient (r) = 0.99999

Weighting : 1/x

Settings



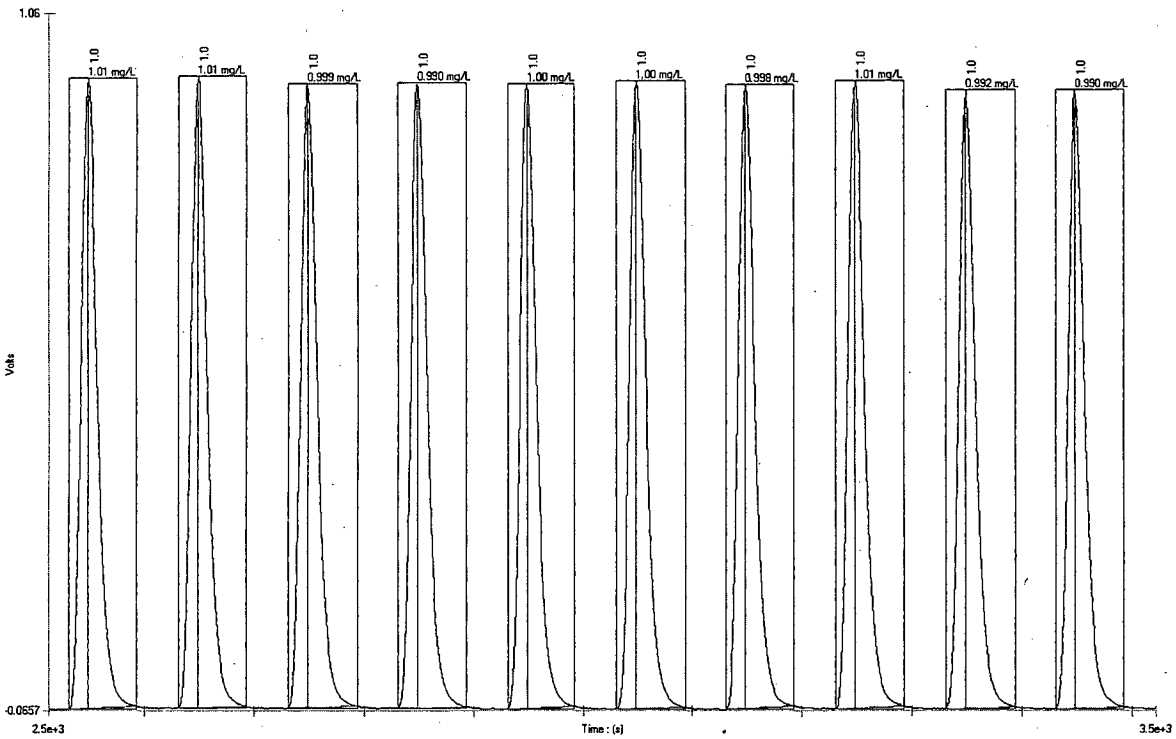
Method Detection Limit for Nitrogen using a 0.02 mg N/L standard

MDL= 0.003 mg N/L

Standard Deviation (s) = 0.00096 mg N/L, Mean (x) = 0.025 mg N/L, Known Value = 0.02 mg N/L

File Name: OM_11-19-2007_12-48-56PM.OMN

Acq. Date: 19 Nov 2007



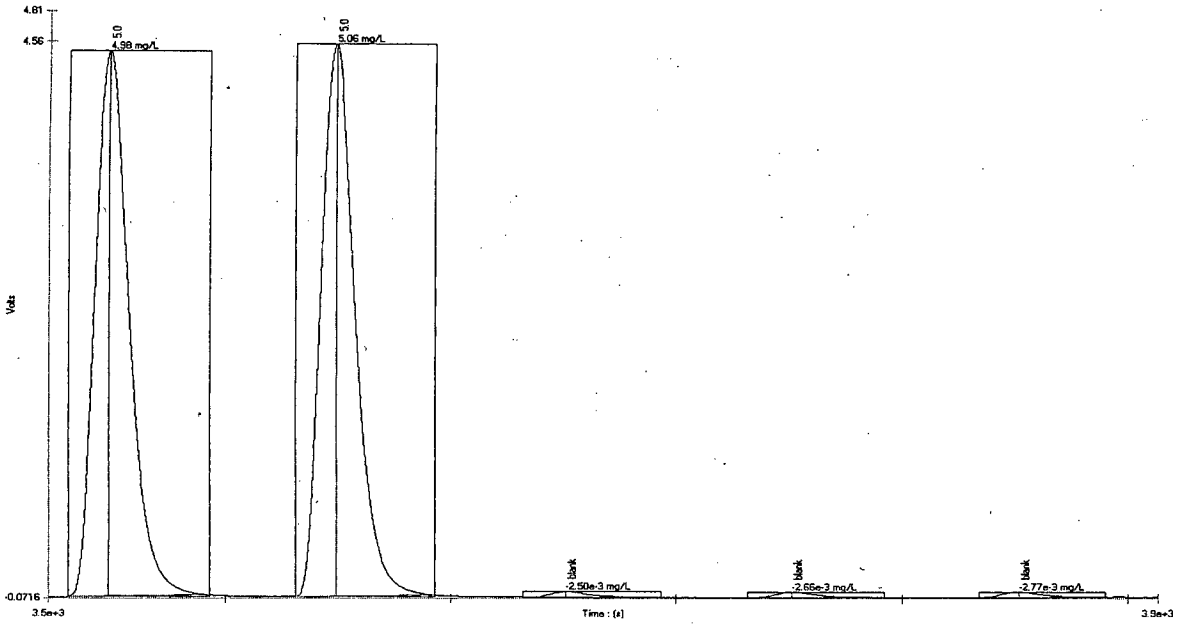
Precision Data for Nitrogen using a 1.0 mg N/L standard

% RSD =0.75

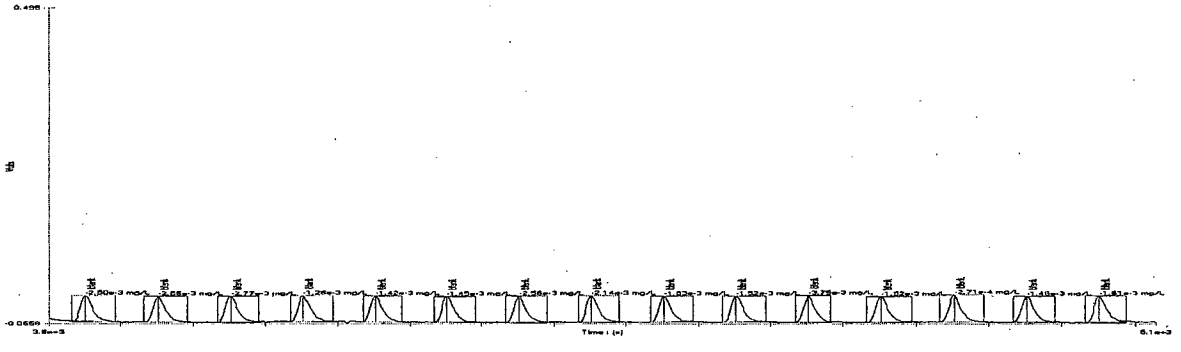
Standard Deviation (s) = 0.0075 mg N/L, Mean (x) = 1.00 mg N/L, Known Value = 1.00 mg N/L

File Name: OM_11-19-2007_12-48-56PM.OMN

Acq. Date: 19 Nov 2007



Carryover Study:
Two 5.0 mg N/L standards followed by three blanks
Carryover Passed
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007



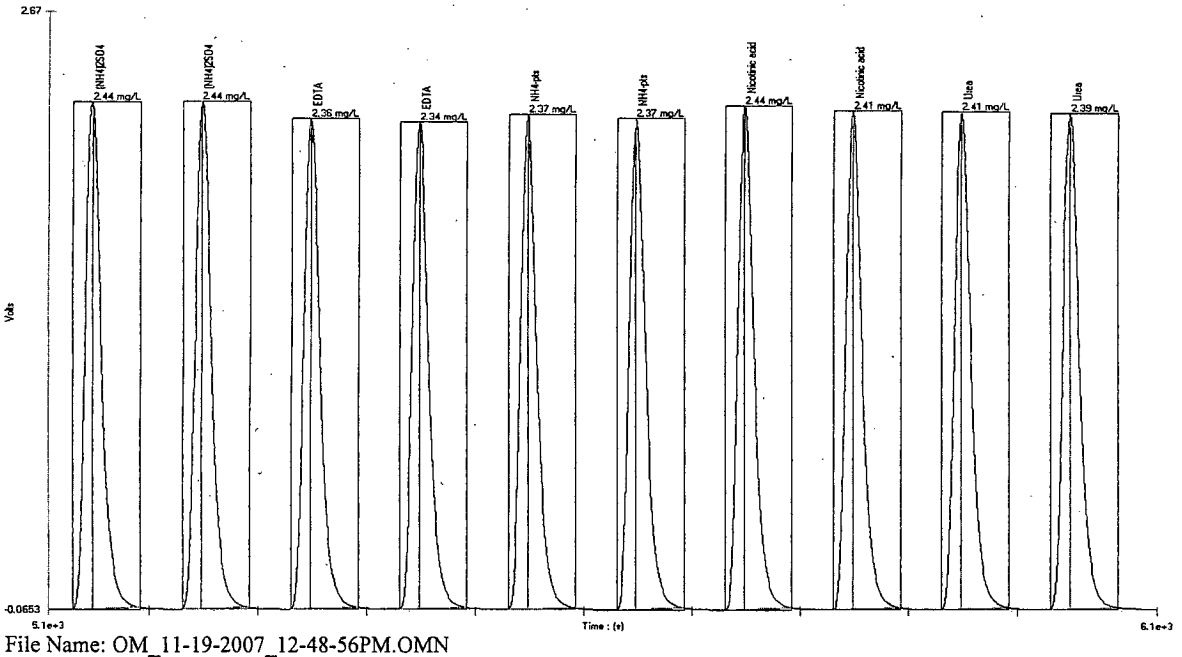
DIN Blanks

Average: -0.00191 mg N/L, SD = 0.00083 mg N/L. Calculated DIN Limits: Detection Limit = 0.0025 mg N/L, Decision Limit = 0.005 mg N/L, Determination Limit = 0.0075 mg N/L.
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

Digestion Efficiency for Nitrogen containing compounds in DI water at 2.5 mg N/L

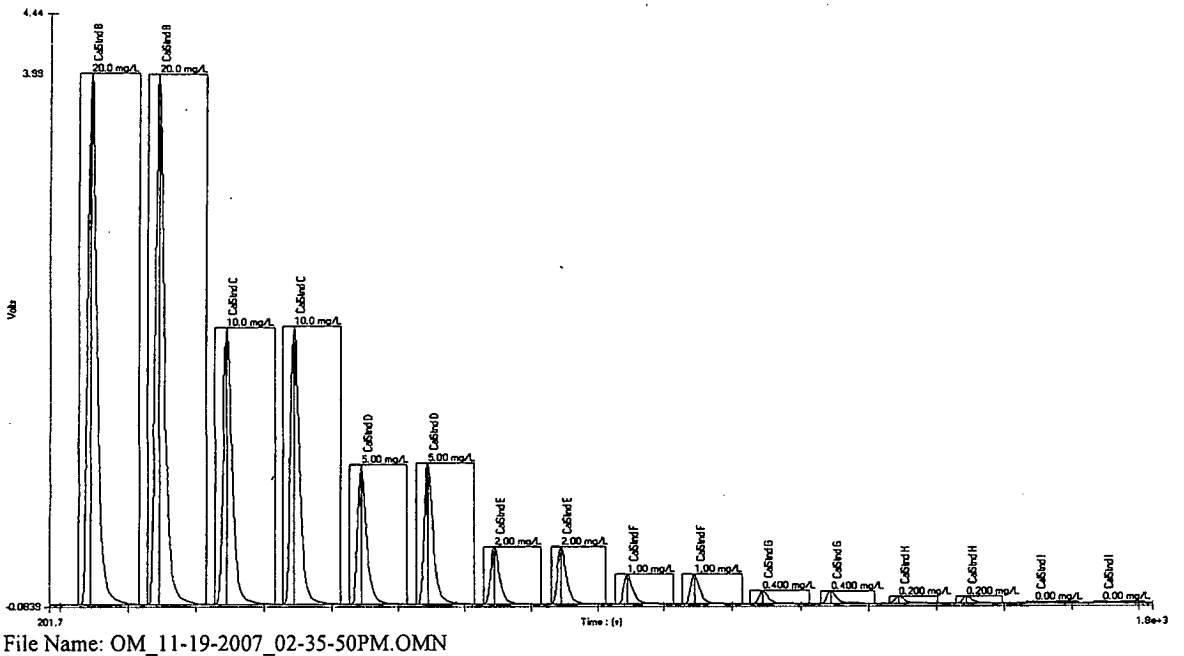
Nitrogen Form	Mean Result (mg N/L)	%Recovery
Ammonia	2.44	97.6
EDTA	2.35	94.0
NPTS*	2.37	94.8
Nicotinic Acid	2.43	97.0
Urea	2.40	96.0

* Ammonium p-toluenesulfonate



File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

Calibration Data for Total Nitrogen High Range



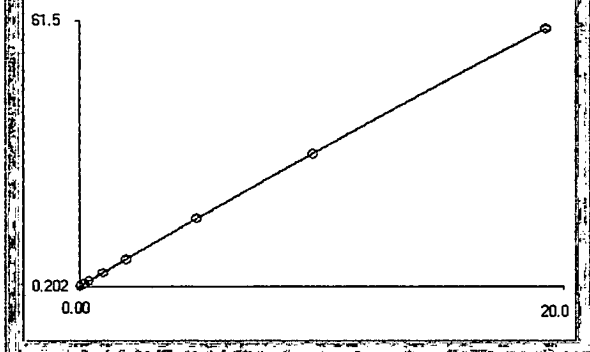
File Name: OM_11-19-2007_02-35-50PM.OMN
Acq. Date: 19 Nov 2007

Calibration Graph and Statistics

Calibration Results - Channel 1

TN

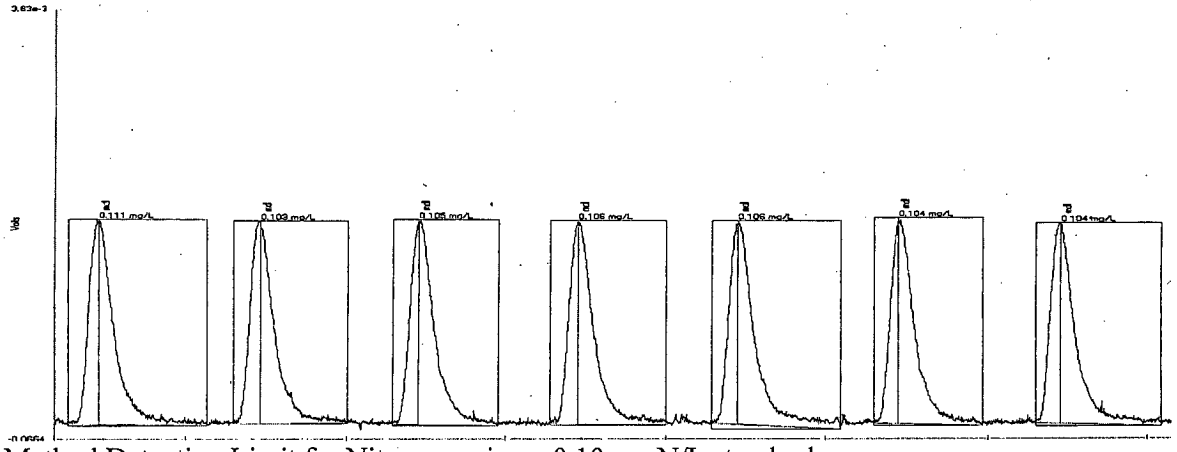
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	61.5	4.05	0.3	-0.2	☐	20.0	11/19/2007	2:39:32 PM
2	20.0	2	61.2	4.05	0.3	0.2	☐	20.0	11/19/2007	2:41:10 PM
3	10.0	1	31.7	2.11	0.1	0.3	☐	9.98	11/19/2007	2:42:47 PM
4	10.0	2	31.8	2.12	0.1	0.1	☐	10.0	11/19/2007	2:44:25 PM
5	5.00	1	16.3	1.07	0.6	-0.2	☐	5.01	11/19/2007	2:46:03 PM
6	5.00	2	16.4	1.08	0.6	-1.1	☐	5.05	11/19/2007	2:47:41 PM
7	2.00	1	6.66	0.441	1.1	0.5	☐	1.99	11/19/2007	2:49:17 PM
8	2.00	2	6.56	0.437	1.1	2.0	☐	1.96	11/19/2007	2:50:54 PM
9	1.00	1	3.48	0.228	0.3	-0.4	☐	1.00	11/19/2007	2:52:31 PM
10	1.00	2	3.49	0.229	0.3	-0.9	☐	1.01	11/19/2007	2:54:08 PM
11	0.400	1	1.56	0.0991	2.8	-3.5	☐	0.416	11/19/2007	2:55:46 PM
12	0.400	2	1.50	0.0970	2.8	0.6	☐	0.397	11/19/2007	2:57:25 PM
13	0.200	1	0.851	0.0538	0.2	1.1	☐	0.197	11/19/2007	2:59:04 PM
14	0.200	2	0.854	0.0541	0.2	0.8	☐	0.198	11/19/2007	3:00:42 PM
15	0.00	1	0.211	0.0112			☐	1.42e-3	11/19/2007	3:02:20 PM
16	0.00	2	0.202	0.0111			☐	-1.27e-3	11/19/2007	3:03:59 PM



Area = -0.0104 * Conc^2 + 3.26 * Conc + 0.208
Conc = 3.53e-4 * Area^2 + 0.305 * Area - 0.0631
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



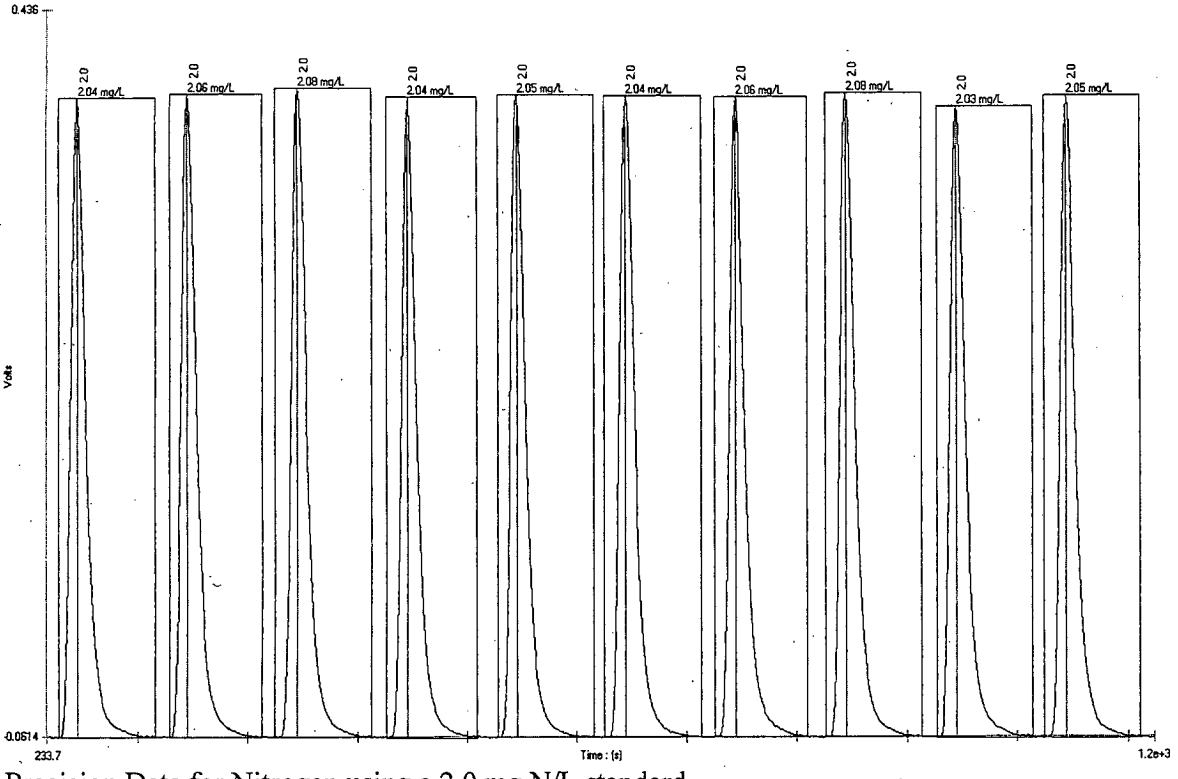
Method Detection Limit for Nitrogen using a 0.10 mg N/L standard

MDL= 0.008 mg N/L

Standard Deviation (s) = 0.0026 mg N/L, Mean (x) = 0.106 mg N/L, Known Value = 0.10 mg N/L

File Name: OM_11-19-2007_02-35-50PM.OMN

Acq. Date: 19 Nov 2007



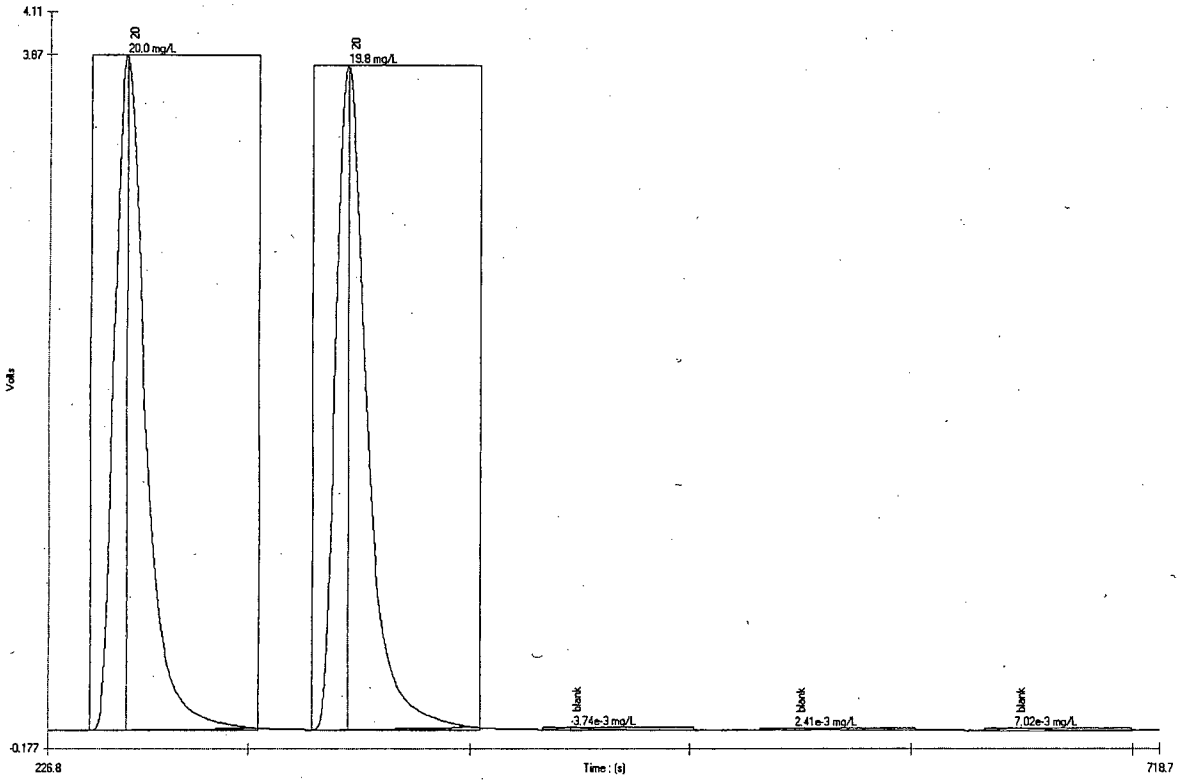
Precision Data for Nitrogen using a 2.0 mg N/L standard

% RSD =0.85

Standard Deviation (s) = 0.0174 mg N/L, Mean (x) = 1.05 mg N/L, Known Value = 2.00 mg N/L

File Name: OM_11-20-2007_07-25-01AM.OMN

Acq. Date: 20 Nov 2007



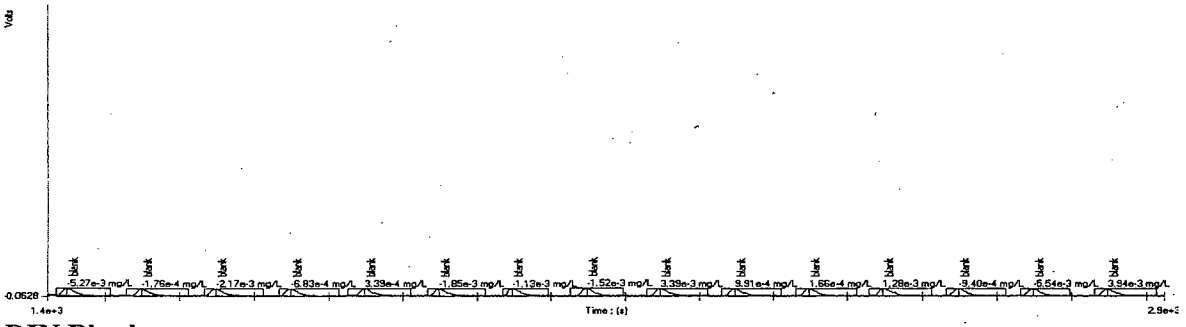
Carryover Study:

Two 20.0 mg N/L standards followed by three blanks

Carryover Passed

File Name: OM_11-26-2007_09-09-11AM.OMN

Acq. Date: 26 Nov 2007



DIN Blanks

Average: -0.00061 mg N/L, SD = 0.0026 mg N/L. Calculated DIN Limits: Detection Limit = 0.0078 mg N/L, Decision Limit = 0.0157 mg N/L, Determination Limit = 0.0235 mg N/L.

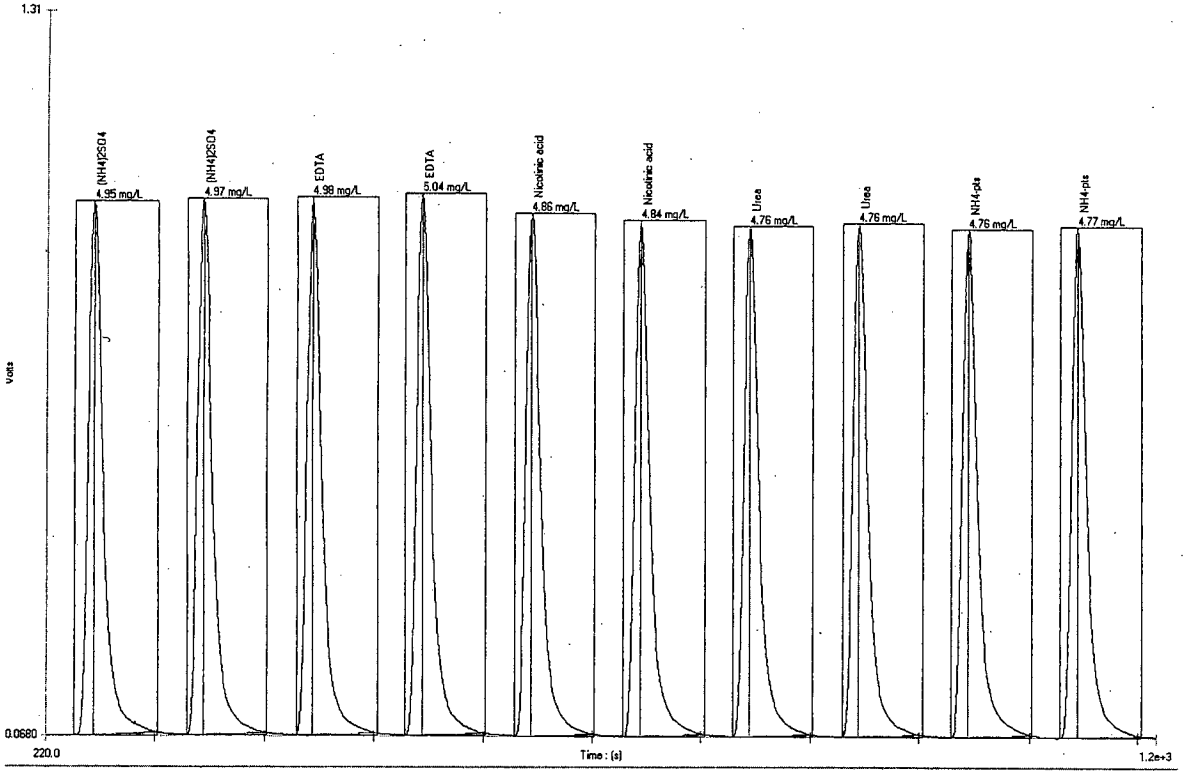
File Name: OM_11-20-2007_07-25-01AM.OMN

Acq. Date: 20 Nov 2007

Digestion Efficiency for Nitrogen containing compounds in DI water at 5.0 mg N/L

Nitrogen Form	Mean Result (mg N/L)	%Recovery
Ammonia	4.96	99.2
EDTA	5.01	100.2
Nicotinic Acid	4.85	97.0
Urea	4.76	95.2
NPTS*	4.77	95.3

* Ammonium p-toluenesulfonate



File Name: OM_11-26-2007_10-41-56AM.OMN
Acq. Date: 26 Nov 2007

Spike recovery of Total Nitrogen in Wastewater

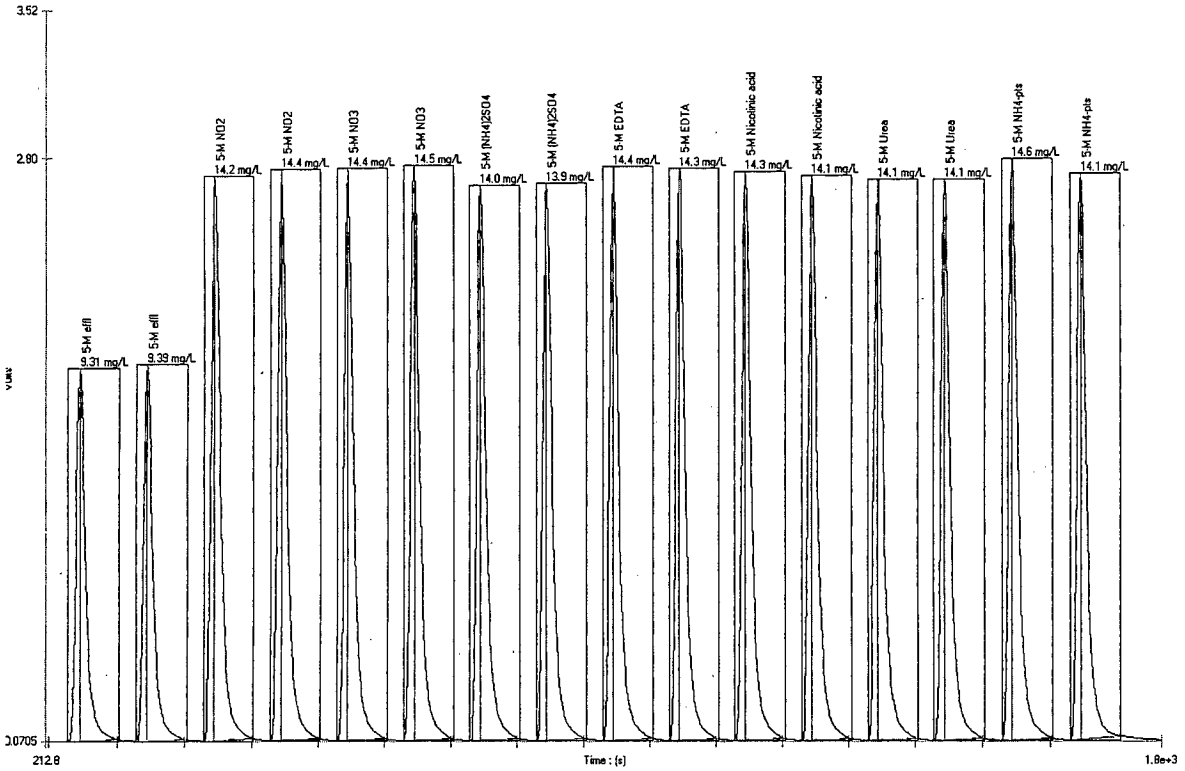
Initial total nitrogen concentration of wastewater was 9.35 mg N/L

Spiking level is 5.0 mg/L of each of the nitrogen compounds listed below:

Nitrogen Compound	Spiked (mg N/L)	Spike Recovery
Nitrite	14.30	99.0%
Nitrate	14.45	102.0%
Ammonia	13.95	92.0%
EDTA	14.35	100.0%
Nicotinic Acid	14.20	97.0%
Urea	14.10	95.0%
NPTS*	14.35	100.0%

* Ammonium p-toluenesulfonate

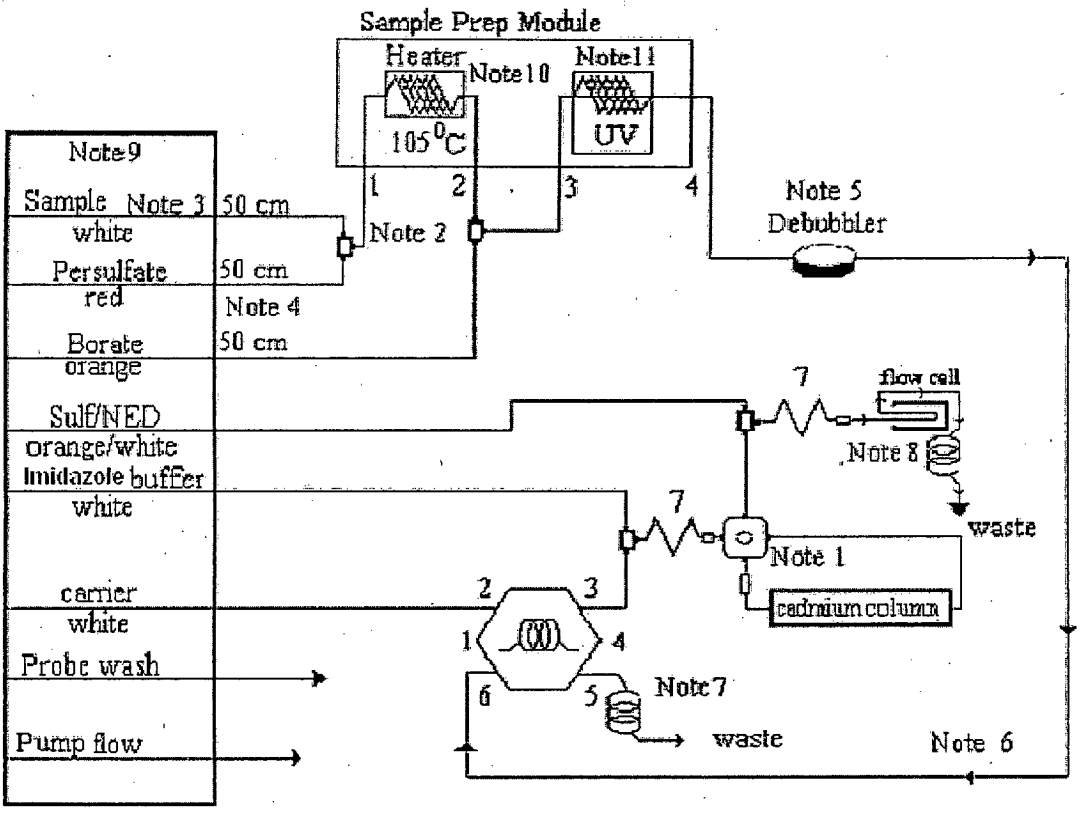
Conclusion: Spike recoveries of 92-102% were obtained using this method.



File Name: OM_11-26-2007_02-09-45PM.OMN

Acq. Date: 26 Nov 2007

17.3. TOTAL NITROGEN MANIFOLD DIAGRAM

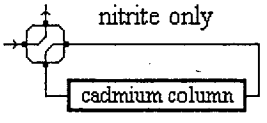


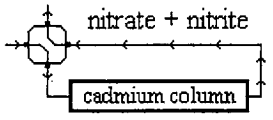
Carrier: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000/8500 Sample Loop: 50 cm Low Range
13 cm High Range (0.5 mm (0.022 in) i.d.)
Interference Filter: 540 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 1200 cm of tubing wrapped around the heater block at the specified temperature.

7: **135** cm of tubing on a 7 cm coil support

Note 1: This is a two state valve used to place the cadmium column in-line with the manifold.





Note 2: Tee's **'1'**and **'2'** are mounted on left side of manifold board.
Note 3: **From sampler to tee fitting '1':** The **white pump tube** is cut 2 cm outside of the tabs on both sides. The outlet of the sample pump tube is connected to tee fitting '1' with **50** cm of 0.8 mm id manifold tubing.

Note 4: **Persulfate (red) and borate (orange) pump tubes** are connected to tees **'1'** and **'2'** with **50** cm lengths of 0.8 mm id manifold tubing.

Note 5: **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. Please note that condensation may form at the outlet of this debubbler. A truly failed membrane will leak around the edge of the disc, not only through these ports.

Note 6: If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of the debubbler connected to Port 6 of the valve.

Note 7: The **100 cm back pressure loop** is 0.5 mm (0.022in.) i.d. tubing.

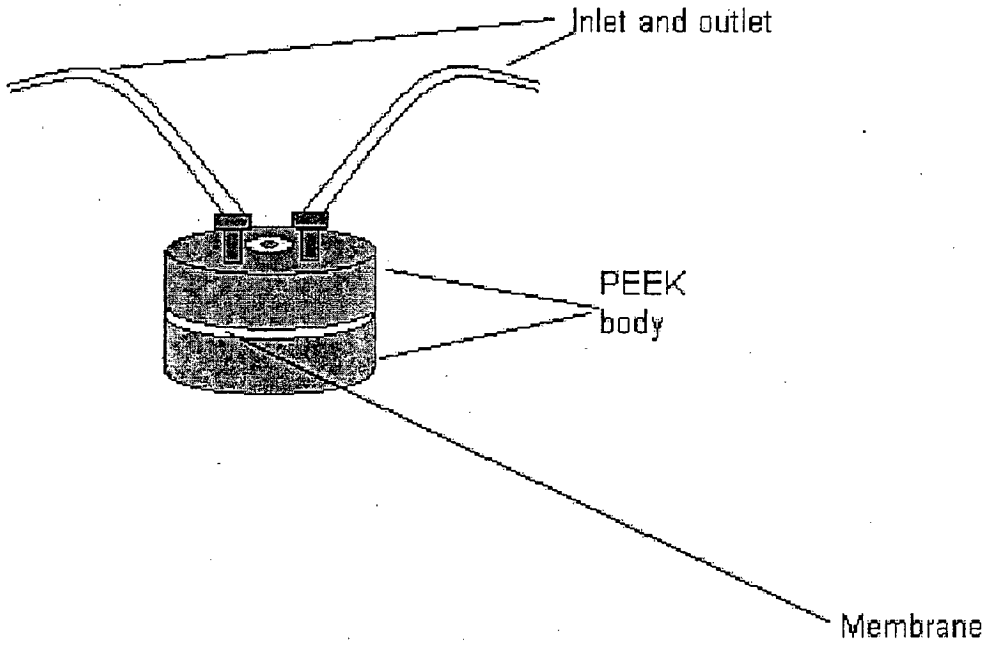
Note 8: The **200 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

Note 9: **PVC PUMP TUBES MUST BE USED FOR THIS METHOD.**

Note 10: Heater (inside of the sample prep module): 1200 cm of 0.032" i.s. manifold tubing tubing is wrapped on a high temperature heater with **90 cm** remaining for connection at the inlet and outlet. (1380 cm total length) The outlet of tee **'1'** is connected to the heater inlet, and the heater outlet is connect to the inlet of tee **'2'**. Tee's **'1'** and **'2'** are mounted on the chemistry manifold board.

Note 11: The **UV-254 lamp (inside of the sample prep module) has 550 cm** of zeus tubing wrapped around the UV lamp with about **50 cm** of tubing remaining at each end for connections. (650 cm total length) The outlet of tee **'2'** is connected to the UV inlet, and the UV outlet is connected to the tubular membrane debubbler.

17.4. DEBUBBLER:



This debubbler has holes in the bottom, and a circular membrane sandwiched between two round pices of tan PEEK. Typically, it does not require a backpressure loop on the outlet.

→ When a liquid other than water is passed through this debubbling unit, it is very important that DI water be pumped through it for 5-10 minutes, followed by pumping air for another 5-10 minutes at the end of each days run. This aids in removing salts, acids, and bases that could reduce the lifetime of the membrane, and at least partially dries the hydrophobic membrane material. Membranes typically last 1-3 weeks, or even longer with fastidious care.

If the solution passing through the unit is very hot, it is not unusual to see water droplets on the outside. If bubbles are still entering in the fluid stream but not exiting at the outlet, the unit is still properly functioning despite this condensation.

Membranes are replaced by removal of the Allen screw in the center of the block. The "expired" membrane is removed, and a replacement centered. If the replacement membrane has any text on it, the membrane should be placed so that the text side faces the bottom of the unit.
The part numbers for this are as follows:

85362 BUBBLE TRAP, QC8000/8500 (Not salable)
85363 BUBBLE TRAP, SPARE MEMBRANES, PK 5
85364 TUBING SET, BUBBLE TRAP QC8000/QC8500
85361 KIT, BUBBLE TRAP, QC8000/QC8500

17.5. MEASURING NITRATE/NITRITE UTILIZING TN MANIFOLD

17.5.1. DATA SYSTEM PARAMETERS FOR NITRATE/NITRITE

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Low Range

Sample throughput:	60 samples/h, 60 s/sample
Pump Speed:	35
Cycle Period:	60

Analyte Data:

Concentration Units:	mg N/L
Peak Base Width:	67.6 s
Inject to Peak Start:	28.9 s
Chemistry:	Direct/Bipolar

Calibration Data:

Level	1	2	3	4	5	6	7	8	9
Concentration mg N/L	2.00	1.00	0.40	0.20	0.10	0.04	0.02	0.01	0.00

Calibration Fit Type:	2nd Order Polynomial
Weighting Method:	1/x
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	15 s
Sample Period:	20 s

Valve Timing:

Load Period:	15 s
Inject Period:	45 s

High Range

Sample throughput: 45 samples/h, 80 s/sample
Pump Speed: 35
Cycle Period: 80

Analyte Data:

Concentration Units: mg N/L
Peak Base Width: 67.6 s
Inject to Peak Start: 28.9 s
Chemistry: Direct/Bipolar

Calibration Data:

Level	1	2	3	4	5	6	7	8	9
Concentration mg N/L	20.0	10.0	5.00	2.00	1.00	0.40	0.20	0.10	0.00

Calibration Fit Type: 2nd Order Polynomial
Weighting Method: 1/x
Force through zero: No

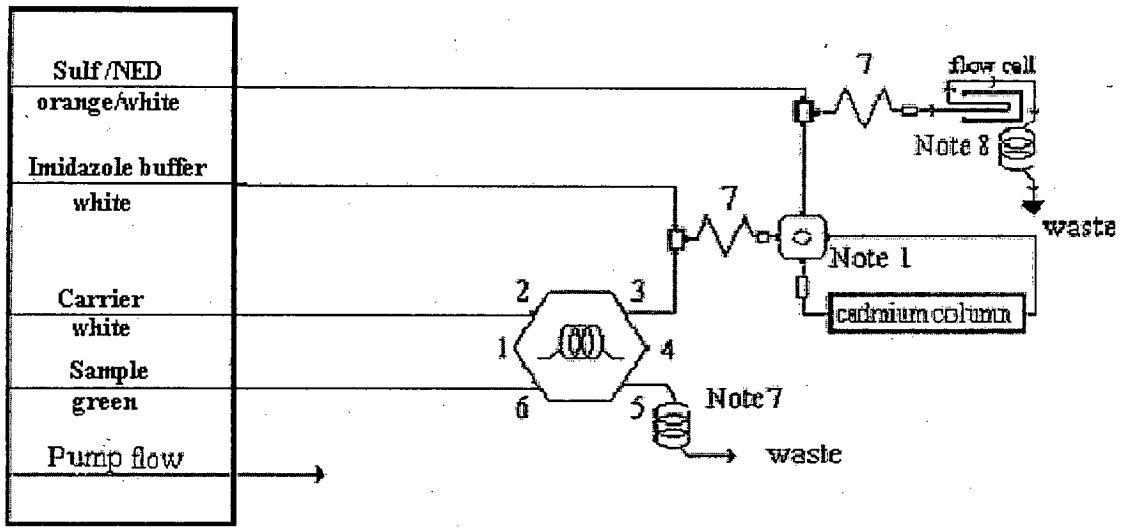
Sampler Timing:

Min. Probe in Wash Period: 15 s
Sample Period: 15 s

Valve Timing:

Load Period: 10 s
Inject Period: 70 s

Nitrate manifold

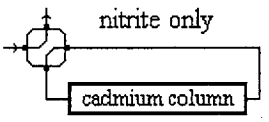


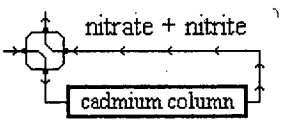
Carrier: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000/8500 Sample Loop: 40 cm Low Range
Microloop High Range
Interference Filter: 540 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

7: **135** cm of tubing on a 7 cm coil support

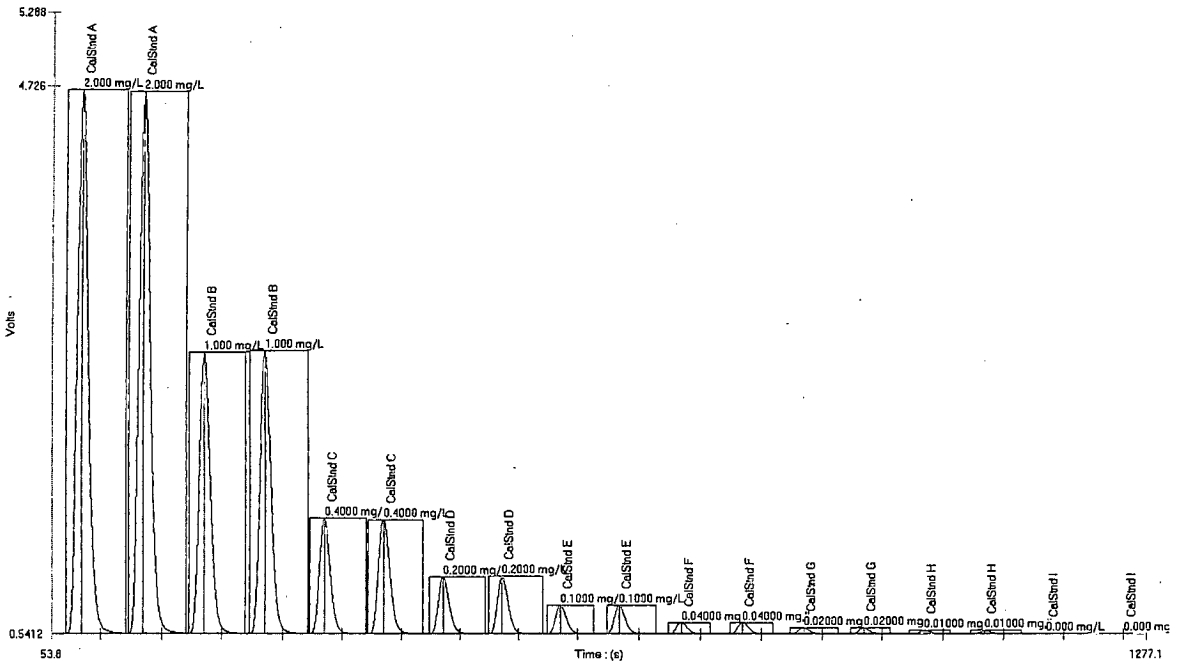
Note 1: This is a two state valve used to place the cadmium column in-line with the manifold.





When changing the in-line manifold over to run for non-digested nitrate/nitrite, you can remove the debubbler from port 6 of the injection valve to speed up the time to valve time.

Calibration Data for Nitrate/Nitrite Low Range



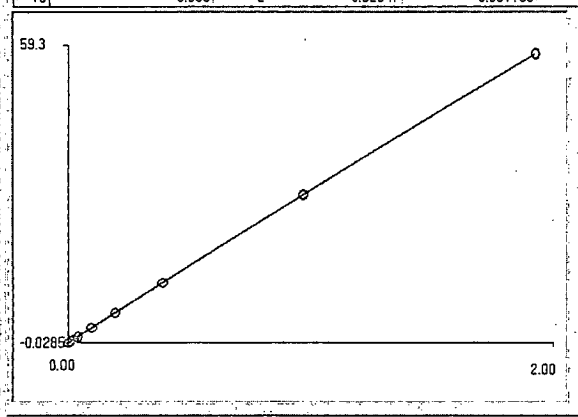
File Name: 12-2 cal support
Acq. Date: 2 Dec 2010

Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

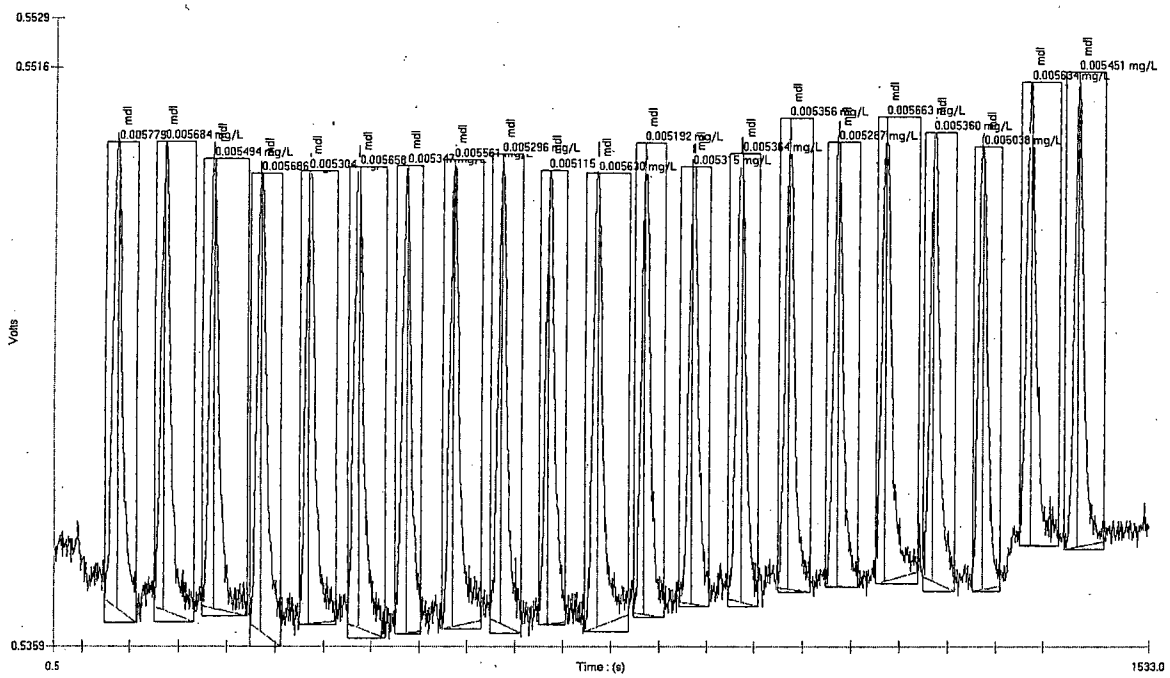
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	2.000	1	59.26	4.156	0.3	-0.2	☐	2.003	12/2/2010	12:01:09 PM
2	2.000	2	59.04	4.141	0.3	0.2	☐	1.995	12/2/2010	12:02:17 PM
3	1.000	1	30.31	2.151	0.4	0.1	☐	0.9992	12/2/2010	12:03:24 PM
4	1.000	2	30.47	2.162	0.4	-0.4	☐	1.004	12/2/2010	12:04:32 PM
5	0.4000	1	12.34	0.8835	0.1	0.0	☐	0.3999	12/2/2010	12:05:39 PM
6	0.4000	2	12.32	0.8753	0.1	0.2	☐	0.3991	12/2/2010	12:06:46 PM
7	0.2000	1	6.165	0.4392	0.4	0.7	☐	0.1983	12/2/2010	12:07:53 PM
8	0.2000	2	6.199	0.4414	0.4	0.2	☐	0.1994	12/2/2010	12:09:00 PM
9	0.1000	1	3.110	0.2218	0.1	0.4	☐	0.09944	12/2/2010	12:10:05 PM
10	0.1000	2	3.107	0.2211	0.1	0.6	☐	0.09934	12/2/2010	12:11:11 PM
11	0.04000	1	1.254	0.08881	0.5	0.9	☐	0.03960	12/2/2010	12:12:20 PM
12	0.04000	2	1.245	0.08799	0.5	1.6	☐	0.03931	12/2/2010	12:13:29 PM
13	0.02000	1	0.6658	0.04667	0.2	-3.3	☐	0.02067	12/2/2010	12:14:37 PM
14	0.02000	2	0.6635	0.04636	0.2	-2.9	☐	0.02060	12/2/2010	12:15:45 PM
15	0.01000	1	0.3566	0.02529	0.6	-6.8	☐	0.01073	12/2/2010	12:16:53 PM
16	0.01000	2	0.3598	0.02513	0.6	-7.7	☐	0.01084	12/2/2010	12:18:01 PM
17	0.000	1	-0.02853	-7.687e-4			☐	-0.001637	12/2/2010	12:19:08 PM
18	0.000	2	0.02047	0.001100			☐	-6.376e-5	12/2/2010	12:20:16 PM



Conc = 2.876e-5 * Area^2 + 0.03211 * Area - 7.210e-4
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



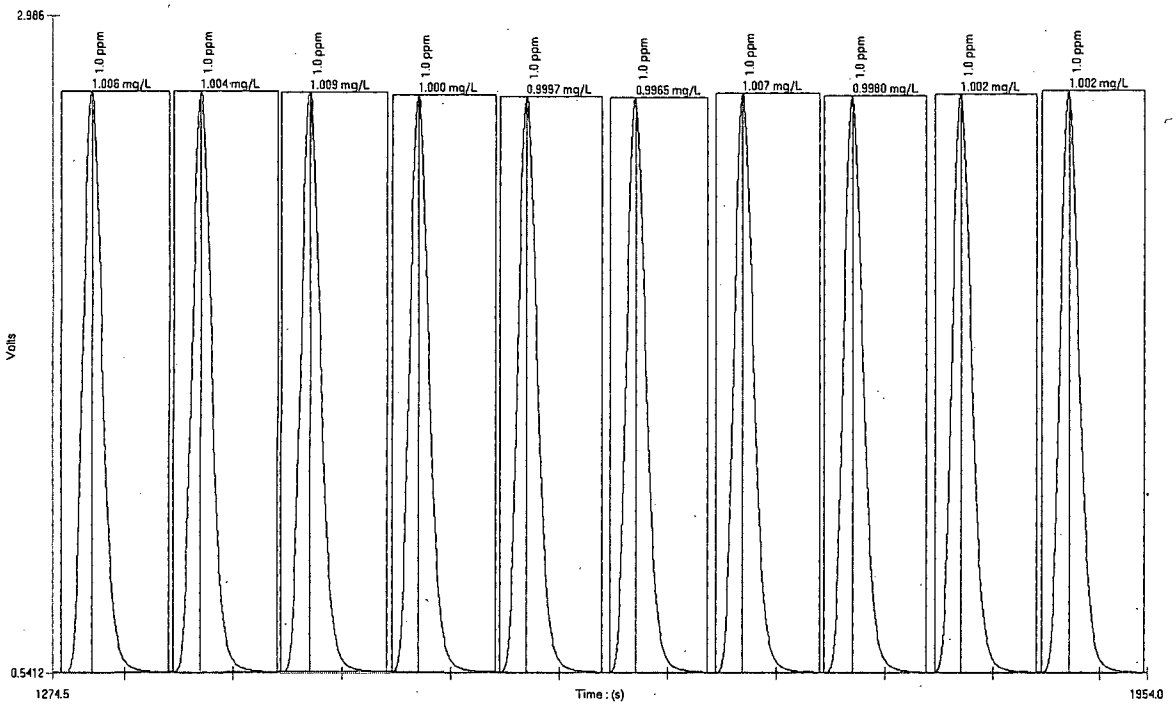
Method Detection Limit for Nitrate/Nitrite using a 0.005 mg N/L standard

MDL= 0.0005 mg N/L

Standard Deviation (s) = 0.0002 mg N/L, Mean (x) = 0.054 mg N/L, Known Value = 0.005 mg N/L

File Name: 12-2 mdl 21

Acq. Date: 2 Dec 2010



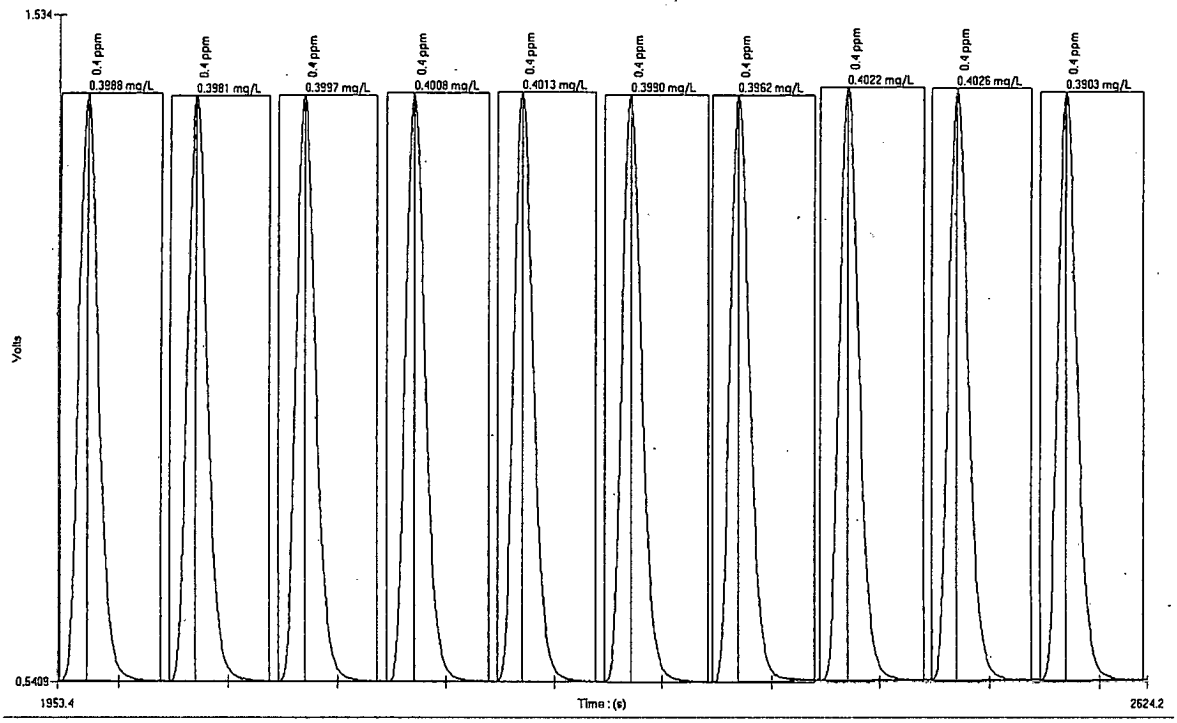
Precision Data for Nitrate/Nitrite using a 1.0 mg N/L standard

% RSD = 0.40

Standard Deviation (s) = 0.004 mg N/L, Mean (x) = 1.00 mg N/L, Known Value = 1.00 mg N/L

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010



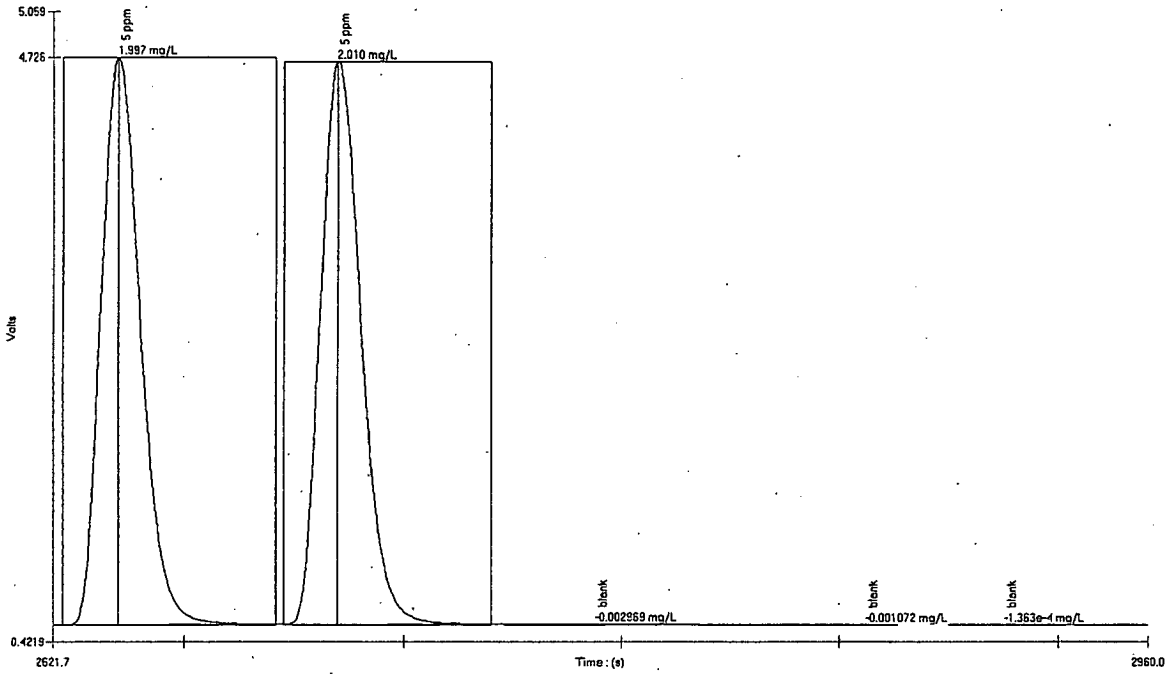
Precision Data for Nitrate/Nitrite using a 0.4 mg N/L standard

% RSD = 0.90

Standard Deviation (s) = 0.0036 mg N/L, Mean (x) = 0.40 mg N/L, Known Value = 0.40 mg N/L

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010



Carryover Study:

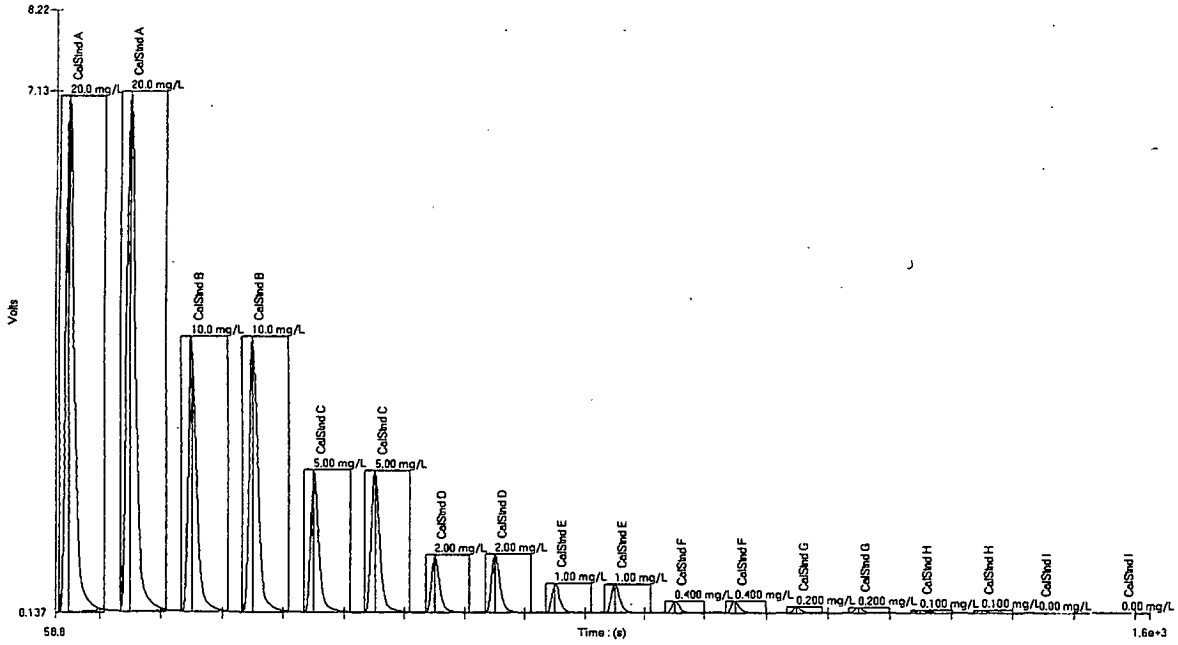
Two 2.0 mg N/L standards followed by three blanks

Carryover Passed

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010

Calibration Data for Nitrate/Nitrite High Range



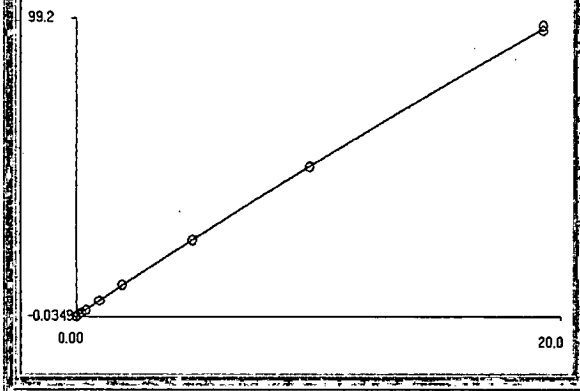
File Name: 11-12 cal HR.omn
Acq. Date: 12 Nov 2009

Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

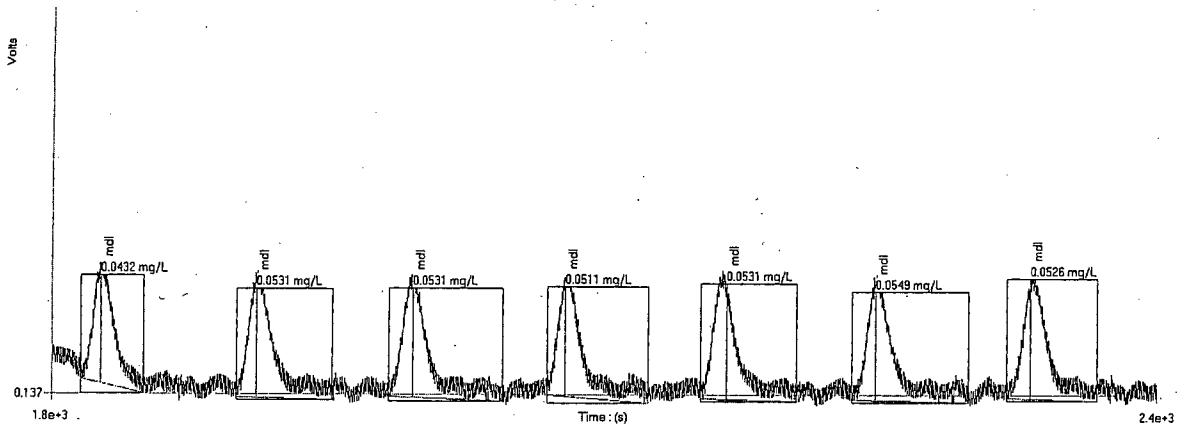
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	97.5	6.92	1.2	0.7	☐	19.8	11/12/2009	7:55:43 AM
2	20.0	2	99.2	6.97	1.2	-1.0	☐	20.2	11/12/2009	7:57:10 AM
3	10.0	1	51.0	3.70	0.4	0.7	☐	9.95	11/12/2009	7:58:39 AM
4	10.0	2	51.3	3.70	0.4	0.1	☐	10.0	11/12/2009	8:00:06 AM
5	5.00	1	26.2	1.91	0.3	0.2	☐	4.99	11/12/2009	8:01:34 AM
6	5.00	2	26.1	1.90	0.3	0.6	☐	4.97	11/12/2009	8:03:01 AM
7	2.00	1	10.7	0.778	1.0	-0.2	☐	2.00	11/12/2009	8:04:29 AM
8	2.00	2	10.8	0.784	1.0	-1.7	☐	2.03	11/12/2009	8:05:56 AM
9	1.00	1	5.41	0.391	0.1	-1.4	☐	1.01	11/12/2009	8:07:23 AM
10	1.00	2	5.40	0.389	0.1	-1.2	☐	1.01	11/12/2009	8:08:49 AM
11	0.400	1	2.16	0.155	0.8	-0.6	☐	0.401	11/12/2009	8:10:15 AM
12	0.400	2	2.16	0.157	0.8	-1.7	☐	0.406	11/12/2009	8:11:42 AM
13	0.200	1	1.06	0.0779	1.2	1.5	☐	0.197	11/12/2009	8:13:10 AM
14	0.200	2	1.08	0.0759	1.2	-0.2	☐	0.200	11/12/2009	8:14:39 AM
15	0.100	1	0.548	0.0389	1.7	-0.9	☐	0.101	11/12/2009	8:16:08 AM
16	0.100	2	0.561	0.0386	1.7	-3.4	☐	0.104	11/12/2009	8:17:36 AM
17	0.00	1	5.10e-3	3.15e-3			☐	3.91e-5	11/12/2009	8:19:05 AM
18	0.00	2	-0.0349	2.07e-3			☐	-7.41e-3	11/12/2009	8:20:33 AM



Area = -0.0221 * Conc^2 + 5.35 * Conc + 7.75e-3
Conc = 1.77e-4 * Area^2 + 0.186 * Area - 9.09e-4
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



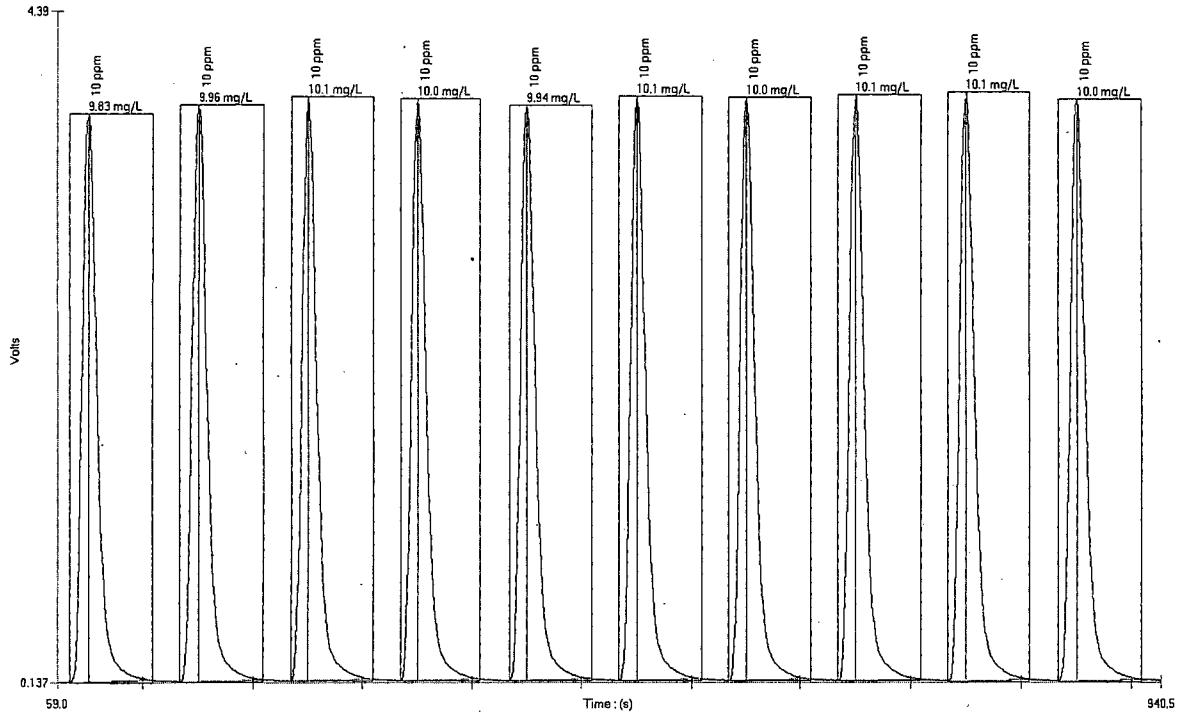
Method Detection Limit for Nitrate/Nitrite using a 0.05 mg N/L standard

MDL= 0.012 mg N/L

Standard Deviation (s) = 0.004 mg N/L, Mean (x) = 0.052 mg N/L, Known Value = 0.05 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009



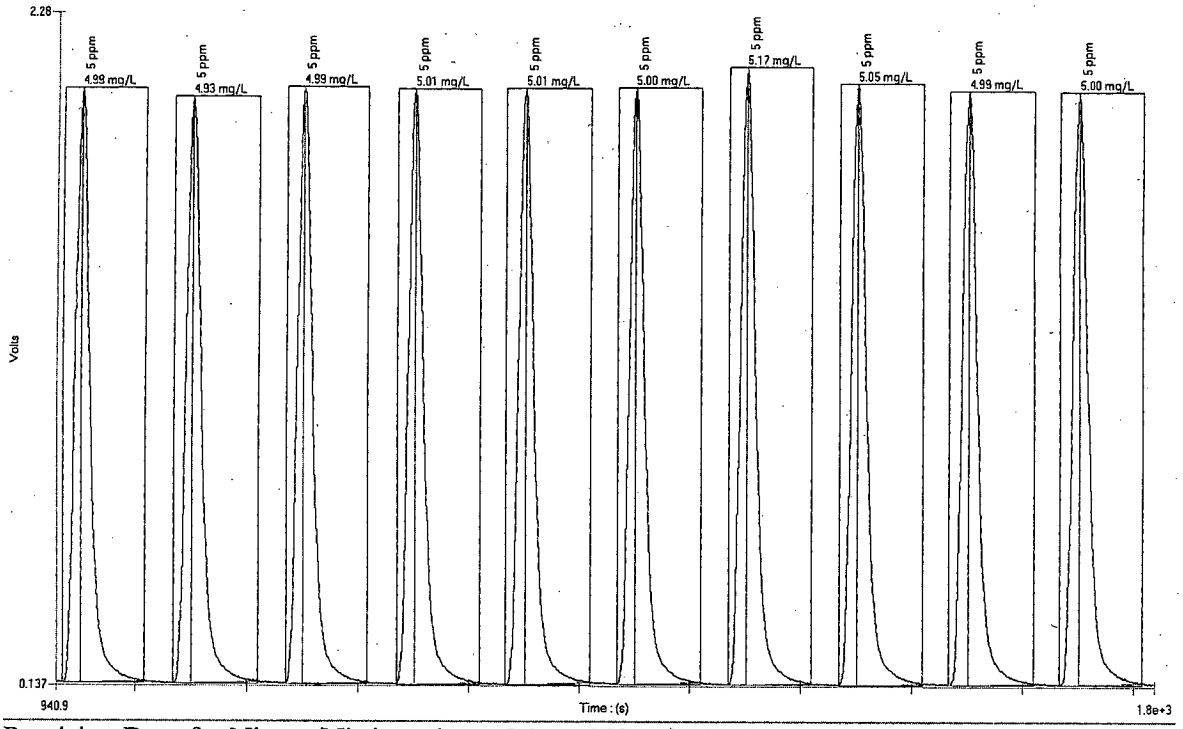
Precision Data for Nitrate/Nitrite using a 10.0 mg N/L standard

% RSD =0.90

Standard Deviation (s) = 0.09 mg N/L, Mean (x) = 10.01 mg N/L, Known Value = 10.0 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009



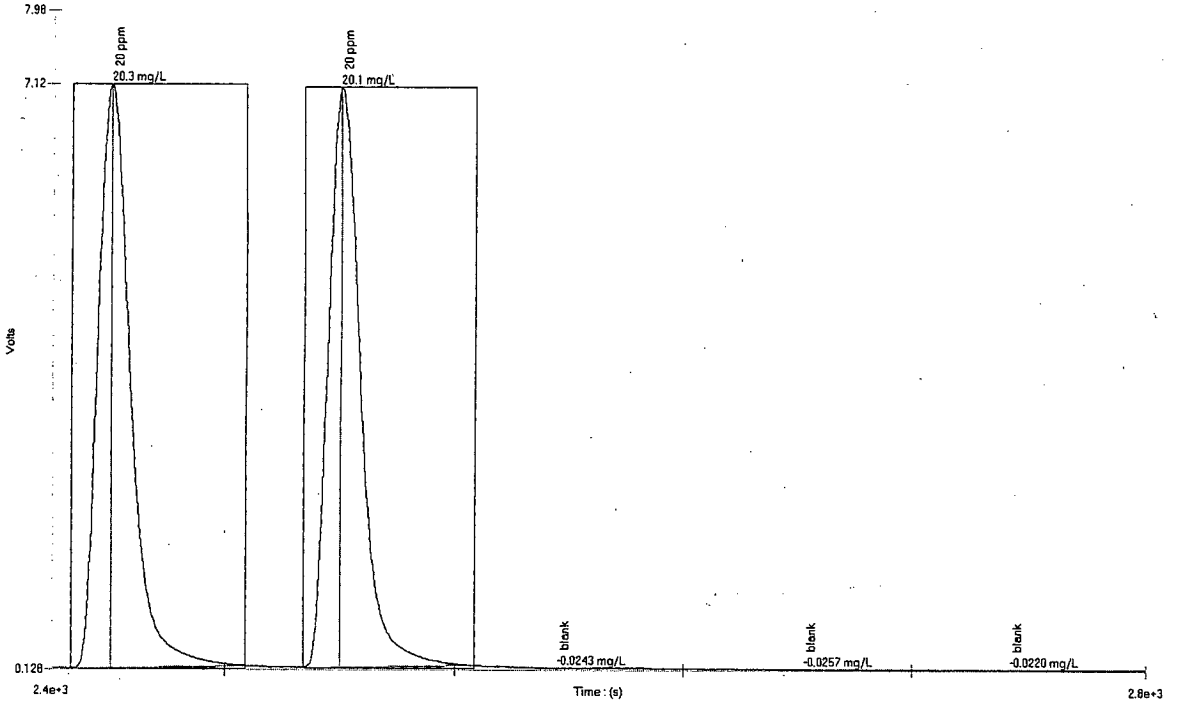
Precision Data for Nitrate/Nitrite using a 5.0 mg N/L standard

% RSD =1.24

Standard Deviation (s) = 0.062 mg N/L, Mean (x) = 5.01 mg N/L, Known Value = 5.00 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009



Carryover Study:

Two 20.0 mg N/L standards followed by three blanks

Carryover Passed

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009

QuikChem® Method 10-115-01-3-E

DETERMINATION OF TOTAL PHOSPHORUS BY FLOW INJECTION ANALYSIS COLORIMETRY (IN-LINE PERSULFATE DIGESTION METHOD)

(Method also includes Manifold Alterations to Analyze Ortho Phosphate)

Written by Lynn Egan

Applications Group

Revision Date:

3 December 2010

LACHAT INSTRUMENTS
5600 LINDBURGH DRIVE
LOVELAND, CO 80539 USA

LACHAT INSTRUMENTS
A Hach Company Brand

QuikChem® Method 10-115-01-3-E

Total Phosphorous (In-Line Persulfate Digestion)

10 to 500 µg P/L

– Principle –

The method is based on the digestion of various phosphorous forms and conversion to phosphate by peroxodisulfate with an in-line UV digestion. Organic phosphorus is converted to orthophosphate by UV catalyzed persulfate digestion. Polyphosphates are converted to orthophosphate by sulfuric acid digestion. The digestion process occurs prior to the sample valve. A portion of the digested sample is then injected and phosphate is determined by FIA.

Wastewater samples are acid preserved and filtered. When this is the case, in-line digestion results match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

After digestion the orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate to form a phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

-Interferences-

1. Silicate is not a significant interference when using this method. 1000 mg/L SiO_2 gives a response of approximately 6 µg P/L.
2. Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

– Special Apparatus –

Please see Parts and Price list for Ordering Information

1. Lachat sample preparation module, A30**X**03 **X** =1 for 110V, **X**=2 for 220V) with UV-254 nm lamp.
2. Heater
3. PVC PUMP TUBES MUST BE USED FOR THIS METHOD.
4. Glass standard and sample vials must be used for this method.

Revised by S. Tucker 3 December 2010. Written and copyrighted © by Lynn Egan on 02 May 2002 by **Lachat Instruments, 5600 Lindburgh Drive, Loveland, CO 80539 USA**. Phone: 970-663-1377 FAX: 970-962-6710.

CONTENTS

QuikChem® Method 10-115-01-3-E

DETERMINATION OF TOTAL PHOSPHORUS BY FIA COLORIMETRY WITH ON-LINE DIGESTION

1. SCOPE AND APPLICATION

1.1. This method covers the determination of total phosphorus in drinking, ground, and surface waters, and domestic and industrial wastes. Wastewater samples are acid preserved and filtered. When this is the case, in-line digestion results match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

1.2. The method of determination is based on reactions that are specific for the orthophosphate (PO_4^{3-}) ion.

1.3. The applicable range is 10 to 500 µg P/L. The statistically determined method detection limit is 1.4 µg P/L. The method throughput is 32 injections per hour.

2 SUMMARY OF METHOD

2.1 The method is based on the digestion of various phosphorous forms to phosphate by peroxodisulfate with an on-line UV digestion. Organic phosphorus is converted to orthophosphate by persulfate digestion catalyzed by UV light. Polyphosphates are converted to orthophosphate by sulfuric acid digestion. The digestion process occurs prior to the sample valve. A portion of the digested sample is then injected and or the phosphates determined by FIA.

2.2 The orthophosphate ion (PO_4^{3-}) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

3. DEFINITIONS

3.1. CALIBRATION BLANK (CB) -- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

3.2. CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.4. LABORATORY SPIKED BLANK (LSB) -- an aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory.

The LSB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5. LABORATORY SPIKED SAMPLE MATRIX (LSM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LSM is analyzed exactly like sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that is digested exactly as a sample including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7. LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.8. MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.9. METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.10. PRACTICAL QUANTITION LIMIT (PQL) -- The lower level where measurements become quantitatively useful is called the PQL. The PQL is defined as PQL = 10∗s, where s = the standard deviation of 21 replicates of a standard 2.5 - 5 times the MDL.

3.11. QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to spike an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.12. STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4. INTERFERENCES

4.1. Silicate is not a significant interference when using this method. 1000 mg/L SiO2 gives a response of approximately 6 µg P/L.

4.2. Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

5.3.1. Sulfuric Acid

5.3.2. Sodium Dodecyl Sulfate (SDS)

5.3.3. Potassium persulfate

5.3.4. antimony potassium tartrate

6. EQUIPMENT AND SUPPLIES

6.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1. Sampler

6.3.2. Multichannel proportioning pump

6.3.3. Reaction unit or manifold

6.3.4. Colorimetric detector

6.3.5. Data system

6.4. Special Apparatus

6.4.1. In-line TN/TP sample prep module with 254 nm lamp.

6.4.2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD.

6.4.3. Glass standard and sample vials must be used with this method.

7. REAGENTS AND STANDARDS

7.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Stock Ammonium Molybdate Solution

By Volume: In a **1 L** volumetric flask, **dissolve 40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24}{\cdot}4H_2O]$ in approximately **800 mL DI water**. Dilute to the mark and mix with a magnetic stirrer for at least four hours. The solution can be stored in plastic for up to two months if refrigerated.

By Weight: To a tared **1 L** container, add **40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24}{\cdot}4H_2O]$ and **983 g DI water**. Mix with a magnetic stirrer for at least four hours. The solution can be stored in plastic for up to two months if refrigerated.

Reagent 2. Stock Antimony Potassium Tartrate Solution

By Volume: In a **1 L** volumetric flask, dissolve **3.22 g antimony potassium tartrate, potassium antimonyl tartrate trihydrate** $C_8H_4O_{12}K_2Sb_2{\cdot}3H_2O$) or **dissolve 3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$) in approximately **800 mL DI water**. Dilute to the mark and mix with a magnetic stirrer until dissolved. The solution can be stored in dark plastic for up to two months if refrigerated.

By Weight: To a **1 L** dark, tared container, **add 3.22 g antimony potassium tartrate, potassium antimonyl tartrate trihydrate** ($C_8H_4O_{12}K_2Sb_2{\cdot}3H_2O$) or **dissolve 3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$) and **995 g DI water**. Mix with a magnetic stirrer until dissolved. The solution can be stored in dark plastic for up to two months if refrigerated.

Reagent 3. Molybdate Color Reagent

By Volume: To a **1 L** volumetric flask, add about **500 mL DI water**, and then add **25 mL Sulfuric Acid** (H_2SO_4). Stir or swirl to mix. Then add **213 mL Ammonium Molybdate Solution** (Reagent 1) and **72 mL Antimony Potassium Tartrate Solution** (Reagent 2). Dilute to the mark and stir to mix. Degas with helium. Prepare weekly, or if blue color or yellow precipitate develops.

By Weight: To a tared **1 L** container, add **690g DI water**, and **47.8 g Sulfuric Acid** (H_2SO_4). Stir or swirl to mix. Then add **213 g Ammonium Molybdate Solution** (Reagent 1) and **72 Antimony Potassium Tartrate Solution** (Reagent 2). Stir to mix. Degas with helium. Prepare weekly or if blue color or yellow precipitate develops.

Reagent 4. Ascorbic Acid Reducing Solution

By Volume: In a **1 L** volumetric flask dissolve **70.0 g granular ascorbic acid** in about **700 mL DI water**. Dilute to the mark and mix with a magnetic stirrer. Degas this

solution with helium. Add **1.0 g SDS** (sodium dodecyl sulfate Aldrich catalog no. 86,201-0). Mix with a magnetic stirrer. Prepare fresh every two days.

By Weight: To a tared **1 L** container, add **70.0 g granular ascorbic acid** and **970 g DI water**. Mix with a magnetic stirrer until dissolved. Degas this solution with helium. **Add 1.0 g SDS** (sodium dodecyl sulfate, Aldrich catalog no. 86,201-0). Mix with a magnetic stirrer. Prepare fresh every two days.

Reagent 5. Sulfuric Acid carrier solution (0.45M)

By Volume: In a **1 L** volumetric flask, add **30 mL sulfuric acid** (H_2SO_4) in **about 600 mL DI water**. Add **9.0 g potassium chloride** (KCl). Dilute to the mark and stir to mix. Degas this solution with helium after the solution is cool. Prepare weekly.

By Weight: To a tared **1 L** container, add **55.2 g sulfuric acid** (H_2SO_4) into **970 g DI water**. **Add 9.0 g potassium chloride** (KCl). Stir to mix. Degas this solution with helium after the solution is cool. Prepare weekly.

7.2. PREPARATION OF DIGESTION REAGENTS

Reagent 6. Digestion Reagent 1

By Volume: To a **1 L** volumetric flask add **500 mL DI water** and then add **106.5 mL sulfuric acid** (H_2SO_4). CAUTION, this solution will become very hot! Dilute to the mark and stir to mix. Allow to cool to room temperature prior to use. Prepare weekly.

By Weight: To a tared **1 L** container, add **893.5 g DI water** and then **add 196.0 g sulfuric acid** (H_2SO_4). CAUTION, this solution will become very hot ! Stir to mix. Allow to come to room temperature before use . Prepare weekly.

Reagent 7. Digestion Reagent 2

By Volume: To a **1 L** volumetric flask add **800 ml DI water** and then **add 26 g potassium persulfate** ($K_2S_2O_8$). Mix with a magnetic stirrer until dissolved. Dilute to the mark. Prepare weekly. Degas before using.

By Weight: To a tared **1 L** container, add **990 g DI water** and then **add 26 g potassium persulfate** ($K_2S_2O_8$). Mix with a magnetic stirrer until dissolved. Prepare weekly. Degas before using.

(Potassium persulfate from EM Science, catalog number PX1560-1, has been shown to give good results with this method.)

7.3. PREPARATION OF STANDARDS

NOTE: Standards are prepared in a matrix of 1.5 mL/L sulfuric acid. This is assumed to match the sulfuric acid added to the samples for preservation. If samples are not preserved, the matrix for the standards is DI water. If a different amount of acid is used for preservation, then standards should be prepared to match the acid level of the samples.

Solution 1. 1.5 ml/L Sulfuric acid:

By Weight: To a tared **4 L** container add **3994 g (mL) DI water** and then add **11.04 g (6 mL) sulfuric acid** (H_2SO_4) and mix.

Standard 1. Stock Standard 250 mg P/L

In a **1 L** volumetric flask **dissolve 1.099 g primary standard grade anhydrous potassium phosphate monobasic** (KH_2PO_4) that has been dried for one hour at 105°C in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare monthly.

Standard 2. Intermediate Stock Standard 1.0 mg P/L

By Volume: In a **1 L** volumetric flask, add about **550 mL solution 1**, and **4.0 mL Stock Standard** (Standard 1). Dilute to the mark with **solution 1**. Invert to mix. Prepare weekly.

By Weight: To a tared **1 L** container add about **4 g Stock Standard** (Standard 1). Divide the actual weight of the solution added by **0.004** and make up to this resulting total weight with **solution 1**. Shake to mix. Prepare weekly.

Working Standards

Working Standards (Prepare Weekly) Concentration mg P/L	**A** 500	**B** 250	**C** 100	**D** 50	**E** 25	**F** 10	**G** 0
By Volume							
Volume (mL) of **stock standard 2** diluted to 250 mL with **solution 1**	125	62.5	25	12.5	---	---	---
Volume (mL) of **Standard D** diluted to 250mL with **Solution 1**	---	---	---	---	125	50	---
By Weight							
Weight (g) of **stock standard 2** diluted to final weight (~250 g) divided by **factor** below with **solution 1**	125	62.5	25	12.5	---	---	---
Weight (g) of **Standard D** diluted to ~250g with **Solution 1**	---	---	---		125	50	---
Division Factor Divide exact weight of the standard by this **factor** to give final weight	0.5	0.25	0.1	0.05	0.5	0.2	---

7.4. PREPARATION OF DIGESTION CHECK STANDARDS

Stock Standard 1. 1000 mg P/L, as phenyl phosphate (PP)

By Volume: In a **1 L** volumetric flask, add **8.20 g phenyl phosphate** ($(C_6H_5OP(O)(ONa)_2\ 2H_2O$, FW = 254.09) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

Stock Standard 2. 1000 mg P/L for trimethyl phosphate (TMP)

By Volume: In a **1 L** volumetric flask, add **4.5 g trimethyl phosphate** ($(CH_3O)_3P(O)$, FW = 140.08) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

Stock Standard 3. 1000 mg P/L for sodium pyrophosphate (2P) ✓

By Volume: In a **1 L** volumetric flask, add **4.292 g sodium pyrophosphate** ($Na_4P_2O_7$ Fw = 265.90) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly. 2.146

Stock Standard 4. 1000 mg P/L for sodium tripolyphosphate (3P)

By Volume: In a **1 L** volumetric flask, add **4.66 g sodium tripolyphosphate 85%,** ($Na_5P_3O_{10}$ FW = 367.86) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

Working Stock Standard Solution 10.0 mg P/L

By Volume: In a **1 L** volumetric flask, about **550 mL Solution 1** (1.5 mL H_2SO_4/L) and **10.0 mL Stock Standard 1, 2, 3, or 4**. Dilute to the mark with **Solution 1**. Invert to mix.

By Weight: To a tared **1 L** container, add about **10 g Stock Standard 1, 2, 3, or 4**. Divide the actual weight of the solution added by **0.01** and make up to this resulting total weight with **Solution 1** (1.5 mL H_2SO_4/L). Shake to mix.

Working Standard	**A**
Concentration µg P/L	500

By Volume

Volume (mL) of **stock standards 1, 2, 3, or 4** diluted to **250 mL** with **Solution 1**	12.5
Volume (mL) of **Standard A** diluted to 250 mL with **Solution 1**	

By Weight

Weight (g) of **stock standards 1, 2, 3, or 4** diluted to final weight (~250 g) divided by **factor** below with **Solution 1**	12.5
Weight (g) of **Standard A** diluted to final weight (~250g) divided by **factor** below with **solution 1**	
Division Factor Divide exact weight of the standard by this **factor** to give final weight	0.05

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and acid rinsed. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

8.2. For NPDES monitoring, samples must be preserved by addition of concentrated H_2SO_4 to pH < 2. This is accomplished by adding no more than 1.5 mL concentrated H_2SO_4 per liter and verifying that the pH is less than 2. If the pH is still greater than 2, more sulfuric acid is added until the pH is < 2. Samples are stored at <6°C. Acid-preserved samples have a holding time of 28 days.

8.3 Samples may be homogenized or sonicated in a device designed for this purpose. However, turbid samples should be filtered since the digestion effectiveness on samples containing particles is unknown.

9. QUALITY CONTROL

9.1.Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated. An analytical batch shall be defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples.

9.1.1. Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in section 9.3.

9.1.2. Analyses of laboratory blanks are required to demonstrate freedom from contamination.

9.1.3. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.4. The laboratory should maintain records to define the quality of data that is generated.

9.2. INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1. Method Detection Limit (MDL) –To establish the ability to detect the analyte, the analyst shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in section 1.2 must be achieved prior to the practice of this method.

9.2.2. Initial Precision and Recovery – To establish the ability to generate acceptable precision results, the operator shall perform 10 replicates of a mid-range standard, according to the procedure beginning in Section 11.

9.2.2.1. Using the results of the replicates compute the average percent recovery (X) and the standard deviation (s) for the analyte. Use the following equation for the calculation of the standard deviation.

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

Where, n = Number of samples, x = concentration in each sample

9.2.2.2. Compare s and x results with the corresponding data in Section 17. If the results meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If however, s and x do not match the data in Section 17, system performance is unacceptable. In this event correct the problem, and repeat the test.

9.3. Matrix spikes- The laboratory must spike, in duplicate, a minimum of 5 percent of all samples (one sample in each batch of no more than twenty samples) from a given sampling site or if for compliance monitoring, from a given discharge. The two sample aliquots shall be spiked with the stock standard (section 7.2).

9.3.1. The concentration of the spike in the sample shall be determined as follows:

9.3.1.1. If, as in compliance monitoring, the concentration of the analyte in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever is higher.

9.3.1.2. If the concentration of the analyte in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard used in Section 9.2.5 or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2. Analyze one sample aliquot out of each set of no more than twenty samples from each site or discharge according to the procedure beginning in Section 11 to determine the background concentration of (B) of the analyte.

9.3.2.1. If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2. Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A)

9.3.3. Calculate the percent recovery (P) of the analyte in each aliquot using the following equation.

$$P = \frac{(A-B)100}{T}$$

Where, A = Measured concentration of analyte after spiking, B = measured background concentration of analyte, T = True concentration of the spike

9.3.4. The percent recovery of the analyte should meet current laboratory acceptance criteria.

9.3.4.1. If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test of the analytical batch is within the current laboratory acceptance criteria, an interference is present. In this case, the results may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be re-sampled. If the interference is attributable to a method deficiency, the analyst must modify the method, repeat the test required in Section 9.1.2 and repeat the analysis of the sample and the matrix spike.

9.3.4.2. If the results of both the spike and ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample reanalyzed.

9.3.5. Compute the relative percent difference (RPD) between two sample results using the following equation:

$$RPD = \frac{(D_1 - D_2)}{(D_1 + D_2)/2} \times 100$$

Where, D1 = Concentration of analyte in the sample, D2 = Concentration of analyte in the second (duplicate) sample.

9.3.6. The RPD for duplicates shall meet the current laboratory acceptance criteria. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

9.4 Laboratory blanks – Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1. Analyze a laboratory reagent water blank initially (with the test in Section 9.2) and with each analytical batch of no more than twenty samples. The blank must be subjected to the same procedural steps as a sample.

9.4.2. If analyte is detected in the blank at a concentration greater than the Minimum Level (Section 1.2), analysis of the samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.5. Calibration Verification – Verify calibration using the procedure described in Section 10

9.6. On-going Precision and Recovery (OPR) – With every analytical batch of no more than twenty samples, a midrange standard must be prepared using the procedure described in Section 11.

9.6.1. Compare the results with the current laboratory acceptance criteria. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

9.7. Quality Control Samples (QCS) – It is suggested that the laboratory obtain and/or prepare a quality control sample using a source different from the source routinely used in section 9.7.1. The QCS is used to verify the concentrations of the calibration standards.

9.8. Depending on the specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

10. CALIBRATION AND STANDARDIZATION

10.1. Prepare a series of at least 3 standards, covering the desired range, and a blank by diluting suitable volumes of standard solution. (See section 7.2.)

10.2. Set up the manifold as shown in Section 17. Calibrate the instrument as described in section 11.

10.3. Prepare standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solution concentration/response data using the computer. Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.

10.4. After the calibration has established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a check standard.

11. PROCEDURE

11.1.1. Prepare a series of standards, covering the desired range, and a blank by diluting suitable volumes of standard solution (suggested range in section 7.3).

11.1.2. Calibrate the instrument as described in section 11.2.

11.1.3. Prepare standard curve by plotting instrument response against concentration values. A calibration curve may be fitted to the calibration solution concentration/response data using the computer. Acceptance or control limits should be established using the difference between the measured value of the calibration solution and the "true value" concentration.

11.1.4. After the calibration has established, it must be verified by the analysis of a suitable quality control sample (QCS). If measurements exceed +/-10% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration must be verified before continuing analysis. Periodic reanalysis of the QCS is recommended as a continuing calibration check.

11.2 CALIBRATION PROCEDURE

11.2.1 Prepare reagent and standards as described in section 5.

11.2.2 Set up manifold as shown in section 12.

11.2.3 Input data system parameters as in section 12.

11.2.4 Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

11.2.5. Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentration, replicates and QC scheme. (See Section 12.)

11.2.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

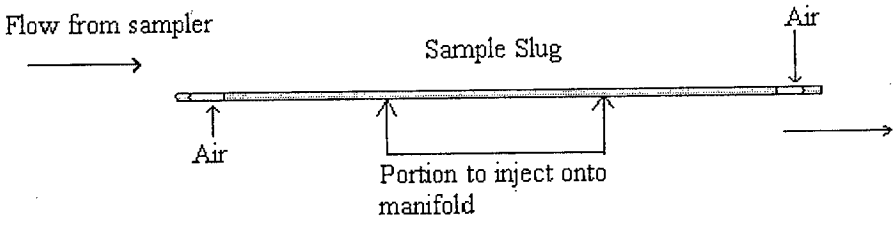
11.3 SYSTEM NOTES

11.3.1. For information on system maintenance and troubleshooting refer to the Lachat Troubleshooting Guide in the System Operation Manual.

11.3.2. Allow more than 20 minutes for the heating unit in the sample prep module to warm to 120°C.

11.3.3. Tubing crimp formation has been observed in the past with the PTFE manifold tubing when no liquid is running through heater tubing and the tubing is allowed to bake. Running liquid (DI or reagents) through the heater whenever the temperature is above 80°C is necessary.

11.3.4. Since the digestion occurs prior to injecting the sample and since there is an air segment between the sample and the sampler wash solution, the valve and sample timing parameters are critical. It is important to verify that center of the sample zone is injected. Timing is verified using Universal dye as the "Sample". (The color will be faded by the digestion reagents). Red food dye (FD&C #40) can also be used for this, as it is decolorized less than the universal dye.



11.3.5. Digestion efficiency should be verified by determining condensed and organic standards at regular intervals.

11.3.6. If experiencing problems with air bubbles on the peaks, change all o-rings in the union fittings between heater, valve, and UV lamp. Change the o-rings in valve, and possibly sample loop if it is crimped. Occasionally, it has been found

necessary to increase the backpressure on the outlet of the debubbler, using a longer length of 0.022" i.d. tubing to connect it to port 6 on the valve, and/or increasing the length of the backpressure coil at port 5. If the membrane begins to weep around the sides, the amount of backpressure is too high. (Condensation at the back of the debubbler is not uncommon)

11.3.7. System Maintenance:

11.3.7.1. Change PVC pump tubing every three days.

11.3.7.2. Change the membrane in the debubbler if it begins to weep around the edges.

11.3.8. Check list before running samples.

11.3.8.1. Check that the method's timing has been correctly set by running food dye.

11.3.8.2. Check the temperature of digestion module.

11.3.8.3. Check that all reagents were prepared correctly.

11.3.8.4. Check that the debubbler is in good condition with no leaking. The debubbler should be tested by running one standard in duplicate or triplicate.

11.3.8.5. If precise duplicate peaks are produced, real samples can be run. Otherwise adjust the timing and troubleshoot further.

11.3.9. Maintain environmental temperature around 20-25°C for best results. If temperature is significantly higher or lower, the heater temperature in the in-line module may need to be adjusted accordingly higher or lower (3-5° to start).

12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

12.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3. Report results in µg P/L.

13. METHOD PERFORMANCE

13.1. The method support data are presented in Section 12. This data was generated according to a Lachat Work Instruction during development of the method.

13.2. Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique play a major role in determining method performance. The support data serves as a guide of the potential method performance.

Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

14. POLLUTION PREVENTION

14.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2. The quantity of chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 115 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1. The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods, and bench operations, complying with the letter and spirit of any water discharge permit and regulations, and by complying with all solid and hazardous waste regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Sect. 14.3.

16. REFERENCES

16.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/R-93-100, Revised March 1993, Method 365.1

16.2. L. Woo, W. Maher, Analytica Chimica Acta 315 (1995) 123-135.

16.3. Guideline and Format for EMSL-Cincinnati Methods. EPA-600/8-83-020, August 1983.

16.4. Richard L. Benson, Ian D. McKelvie and Barry T. Hart, Analytica Chimica Acta 291 (1994) p. 233-242.

16.5. Lachat notebook #133, Ninglan Liao, page 81 to 150.

16.6. Lachat QuikChem Method number 10-115-01-3-A

17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

17.1. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000/8500

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	32 samples/h, 110 s/sample
Pump Speed:	35
Cycle Period:	110

Analyte Data:

Concentration Units:	µg P/L
Chemistry:	Brackish
Inject to brackish baseline start:	20.8
Inject to brackish baseline end:	129.6
Inject to brackish integration start:	40.0
Inject to brackish integration end:	61.0

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration µg P/L	500	250	100	50	25	10	0

Calibration Rep Handling:	Average
Calibration Fit Type:	1st Order Polynomial
Weighting Method:	1/x
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	19 s
Probe in Sample Period:	70 s

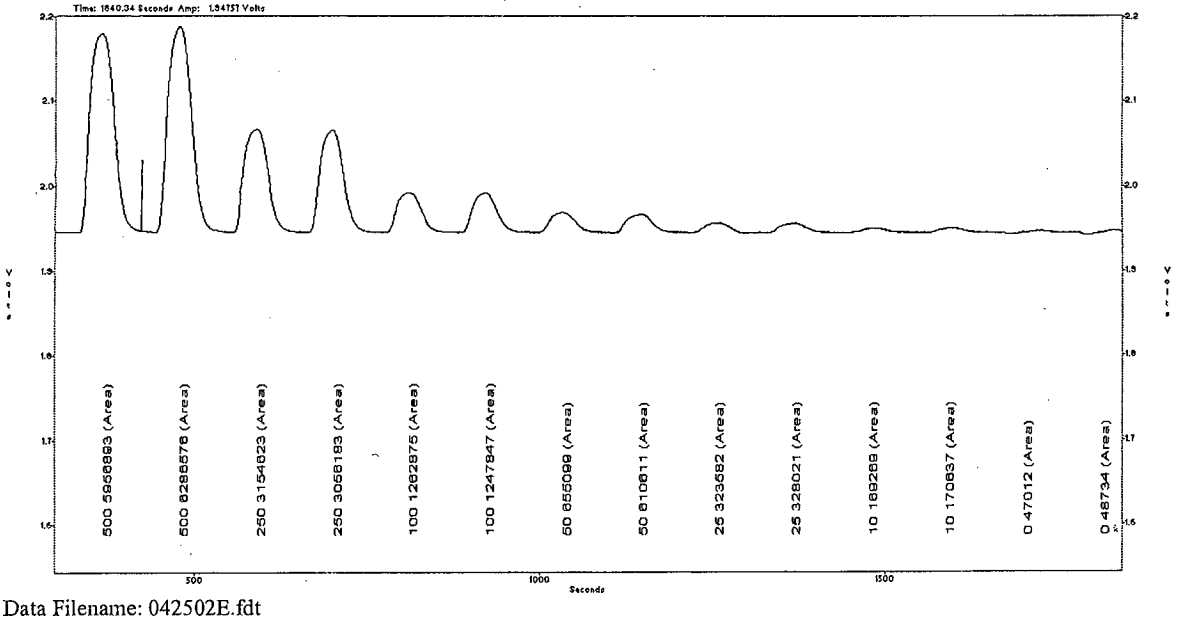
Valve Timing:

Load Period:	35 s
Inject Period:	75 s
Sample to the first valve:	280 s*

Time to first valve must be measured. Value given is as a starting point only.

17.2. SUPPORT DATA FOR QUIKCHEM 8000/8500

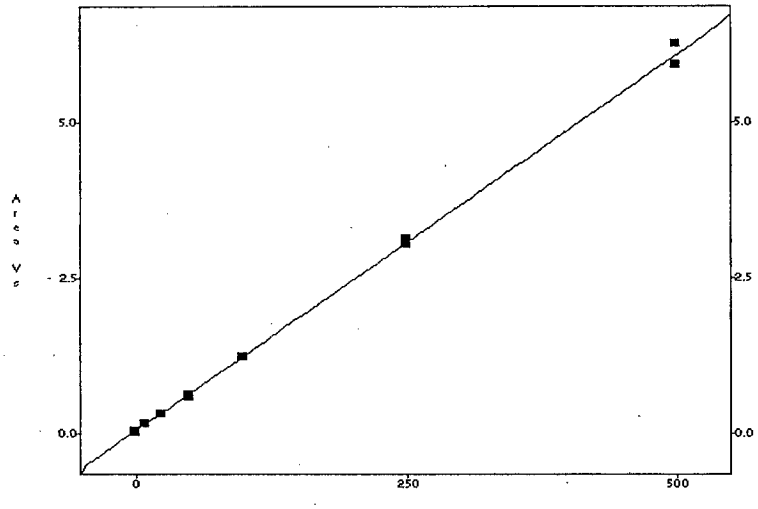
Calibration Data for Total Phosphorus

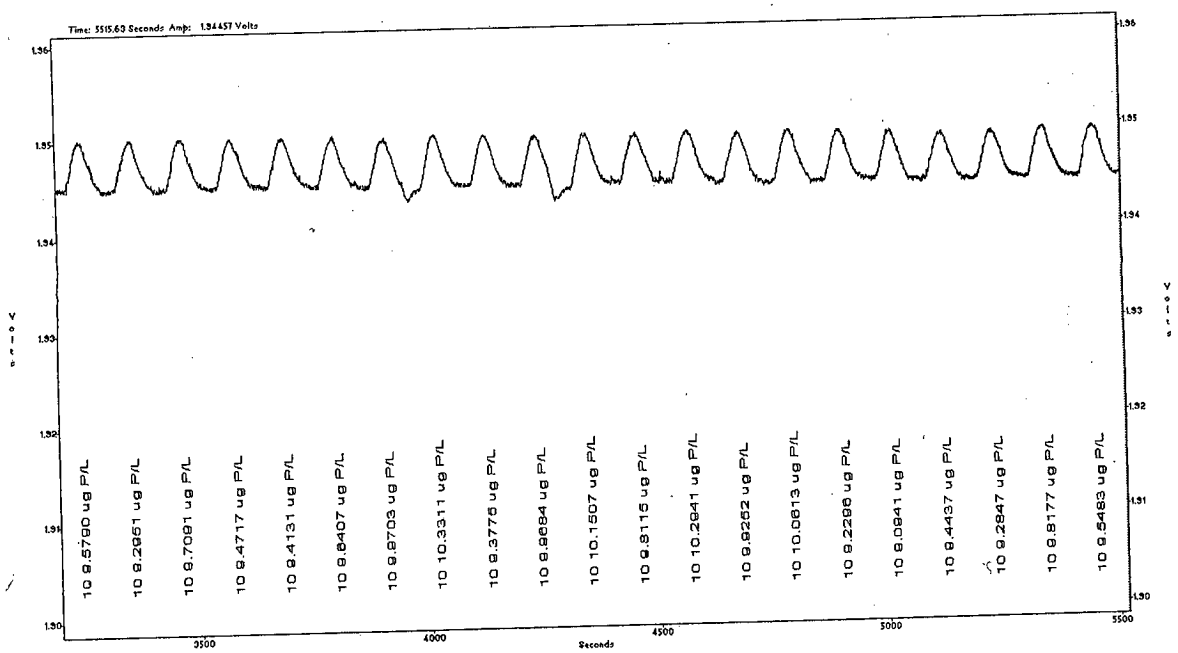


Data Filename: 042502E.fdt
Acq Date: 25 April 2002:

Calibration Graph and Statistics

Level	Area (V-s)	µg P/L	Determined	Rep %RSD	% residual
1	6121734	500	501	3.8	-0.2
2	3105403	250	252.25	2.2	-0.9
3	1255361	100	99.8	0.8	0.2
4	632855	50	48.45	5.0	3.1
5	325801	25	23.18	1.0	7.3
6	169953	10	10.32	0.6	-3.2
7	47873	0	---	2.5	***





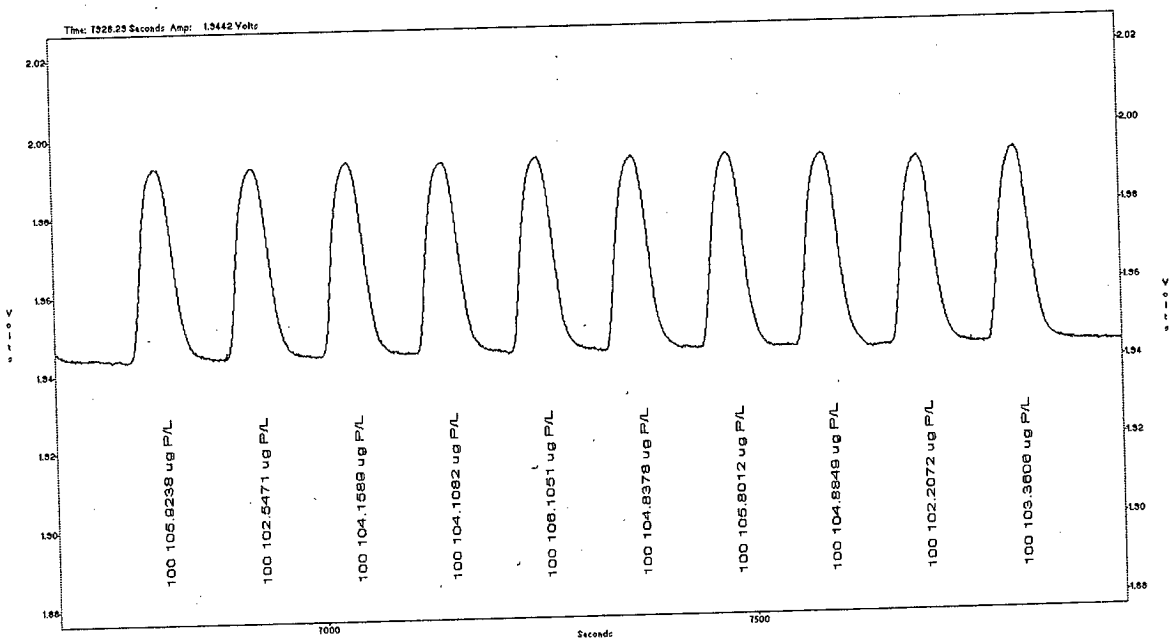
Method Detection Limit using 10 µg P/L as orthophosphate

MDL = 1 µg P/L, claiming 1.4 µg P/L due to carryover

Mean =9.69 µg P/L, Std. Dev. = 0.37 µg P/L, %RSD: 3.71, %residual: 3.1

Data Filename: 042502E.fdt

Acq Date: 25 April 2002:



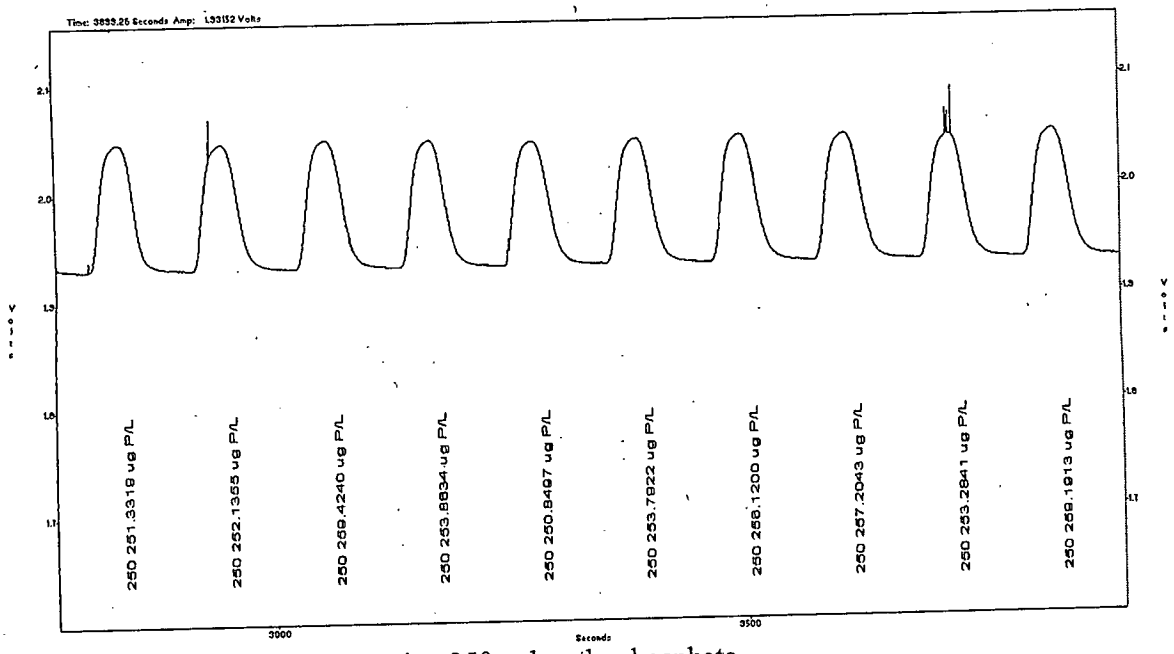
Precision data for phosphorus using 100 ppb orthophosphate

%RSD = 1.32

Mean = 104.39 µg P/L, Std. Dev. = 1.38 µg P/L, %residual: -4.4; known value = 100 µg P/L

Data Filename: 042502E.fdt

Acq Date: 25 April 2002:



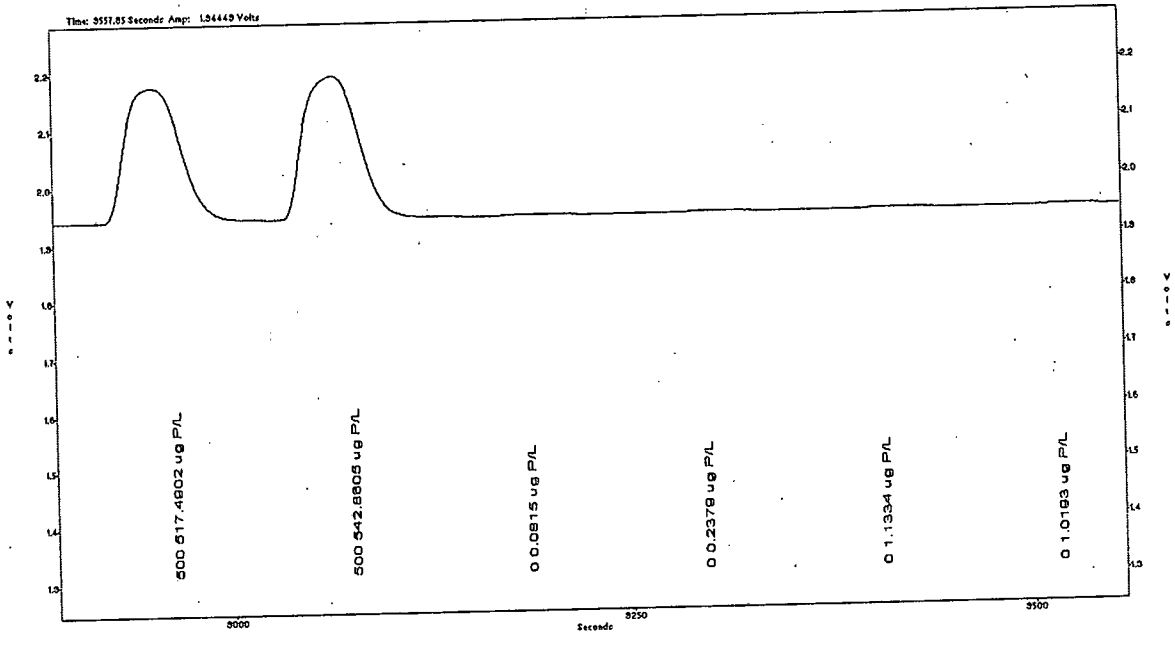
Precision data for phosphorus using 250 ppb orthophosphate

%RSD = 1.22

Mean: 254.72 µg P/L, Std. Dev. = 3.11 µg P/L, known value =250 µg P/L; %residual: -1.89.

Data Filename: 050102A.fdt

Acq Date: 01 May 2002:



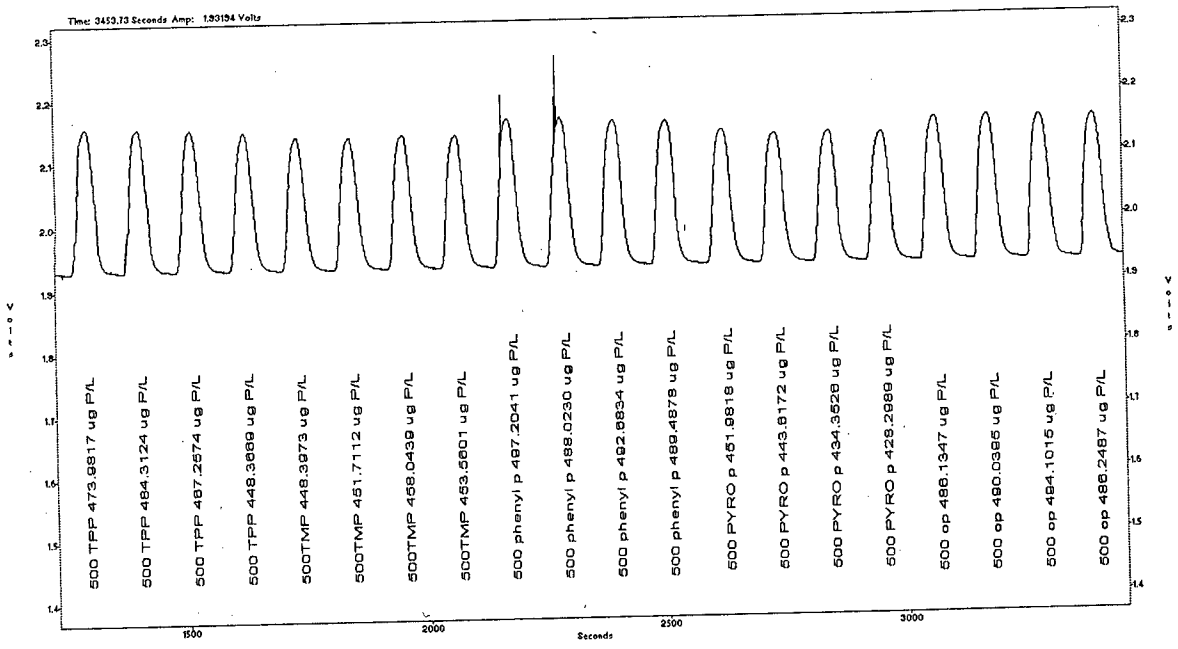
Carryover

Carryover passed

Data Filename: 042502E.fdt

Acq Date: 25 April 2002:

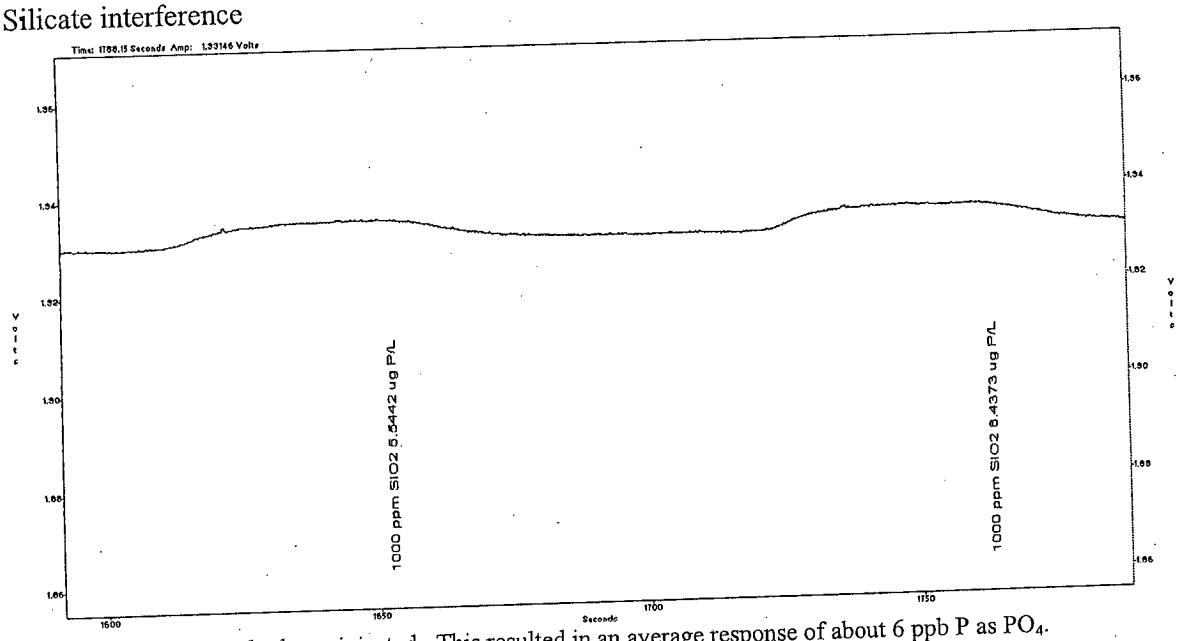
Recovery of Digestion Check Standards at 500 ppb



Data Filename: 050102C.fdt
Acq Date: 01 May 2002:

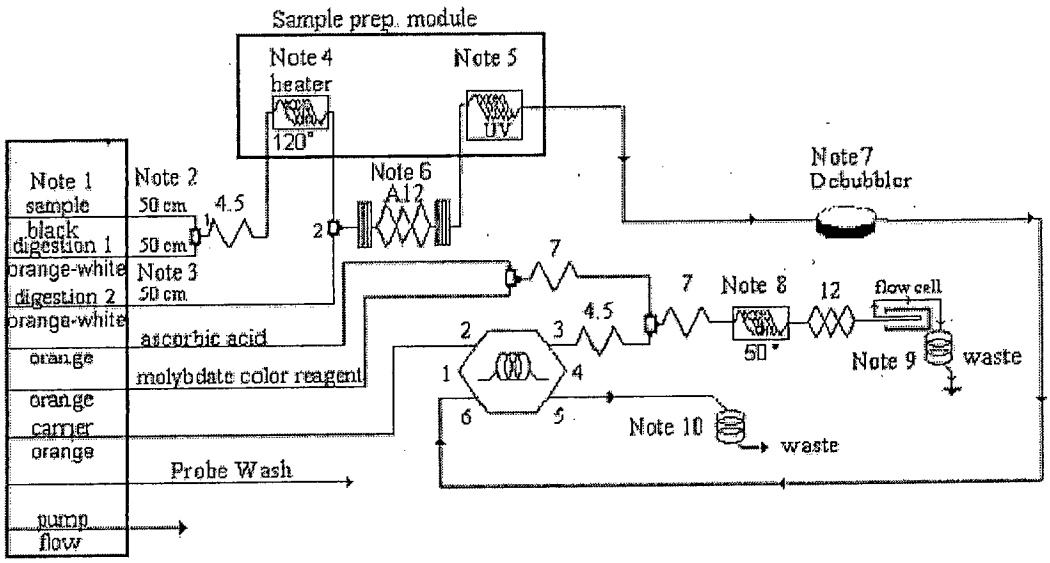
Sample	Known Value, µg P/L	Determined value, µg P/L	% recovery, relative to orthophosphorus
OrthoP	---	489.13	100%
TPP	500	468.48	95.77
Pyro P	500	439.56	89.87
Phenyl Phos	500	491.85	100.55
TMP	500	452.93	92.60

Silicate interference

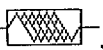


A 1000 ppm SiO_2 standard was injected. This resulted in an average response of about 6 ppb P as PO_4.
Conclusion: Silicate is not a significant interferent in this method. (Selectivity: 166,667)
Data Filename: 050102A.fdt
Acq Date: 01 May 2002

17.3. TOTAL PHOSPHORUS MANIFOLD DIAGRAM



Carrier: **0.45 M Sulfuric acid/KCl solution (Reagent 5).**
Manifold Tubing: **0.5mm (0.022 in) i.d.** This is **2.5 µL/cm**.
QC8000/8500 Sample Loop: 200 cm 0.032" i.d.
Interference Filter: 880 nm

Apparatus: A sample prep module with heater and UV lamp, an injection valve, a 10 mm path length flow cell, a heater  , and a colorimetric detector module are required.

4.5: **70** cm of tubing on a 4.5 cm coil support
7: **135** cm of tubing on a 7 cm coil support
12: **255** cm of tubing on a 12 cm alternating coil support
A12: **150** cm of tubing on a 12 cm aluminum alternating coil support

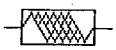
---

Note 1: **PVC PUMP TUBES MUST BE USED FOR THIS METHOD**
Note 2: Tee's **'1'**and **'2'** are mounted on left side of manifold board. **From sampler to tee fitting '1':** The **black pump tube** is cut 3 cm outside of the tabs on both sides. The outlet of the black sample pump tube is connected to tee fitting '1' with **50** cm of 0.8 mm id manifold tubing.
Note 3: **From digestion reagents 1 and 2:** Orange white pump tubes are connected to tee's **'1'** and **'2'** through **50** and **50** cm lengths of manifold tubing.
Note 4: **Heater (inside of the sample prep module):** a total of **880 cm** of 0.032" i.d. manifold tubing is used. **700 cm** is wrapped on a high temperature heater with **90 cm** remaining for connection at the inlet and outlet. The outlet of tee **'1'** is connected to a 4.5 cm coil. The outlet of the coil is connected to the heater inlet, and the heater outlet is connect to the inlet of tee **'2'**. Tee's **'1'** and **'2'** are mounted on the chemistry manifold board.
Note 5: The **UV-254 lamp (inside of the sample prep module) has 450 cm** of zeus tubing (Lachat Part No. 50728) wrapped around the UV lamp with **50 cm** (for a

total of 550 cm) of tubing remaining at each end for connections. The outlet of tee **'2'** is connected to the UV inlet, and the UV outlet is connected to the tubular membrane debubbler.

Note 6: **Aluminum coil support:** Alternating aluminum coil support (A12). The inlet of the A12 is connected to outlet of tee **'2'**, and the outlet is connected to a union, then to UV lamp. Cooling fins are used to keep the coil from becoming too hot. This coil is wrapped with **150 cm** of 0.032 "i.d. (0.8mm) tubing. This coil can be placed on top of the in-line module, if this is convenient. The outlet of the tubular membrane debubbler is connected to port 6 of the valve using a **39 cm** length of **0.5 mm (0.022 in.) i.d.** Teflon tubing.

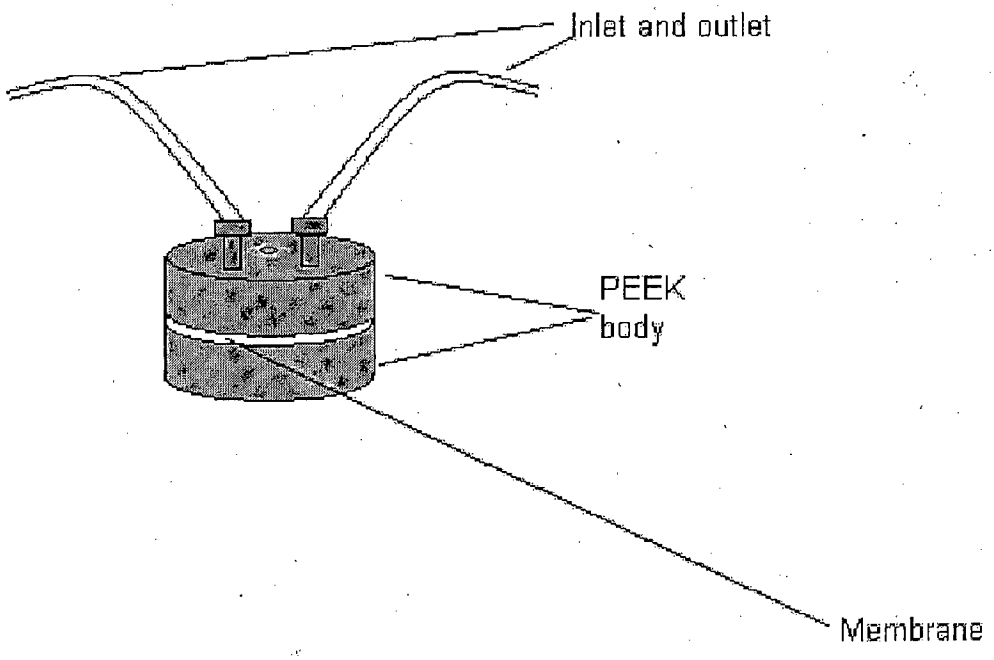
Note 7: **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of the debubbler connected to Port 6 of the valve.

Note 8: The  shows **175 cm** of 0.8 mm i.d. on the heater is used at the temperature shown.

Note 9: **200 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

Note 10: The **100 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

17.4. DEBUBBLER:



This debubbler has holes in the bottom, and a circular membrane sandwiched between two round pieces of tan PEEK. Typically, it does not require a backpressure loop on the outlet.

→ When a liquid other than water is passed through this debubbling unit, it is very important that DI water be pumped through it for 5-10 minutes, followed by pumping air for another 5-10 minutes at the end of each days run. This aids in removing salts, acids, and bases that could reduce the lifetime of the membrane, and at least partially dries the hydrophobic membrane material. Membranes typically last 1-3 weeks, or even longer with fastidious care.

→ If the solution passing through the unit is very hot, it is not unusual to see water droplets on the outside. If bubbles are still entering in the fluid stream but not exiting at the outlet, the unit is still properly functioning despite this condensation.

→ Membranes are replaced by removal of the Allen screw in the center of the block. The "expired" membrane is removed, and a replacement centered. If the replacement membrane has any text on it, the membrane should be placed so that the text side faces the bottom of the unit.
The part numbers for this are as follows:

85362 BUBBLE TRAP, QC8000/8500 (Not salable)
85363 BUBBLE TRAP, SPARE MEMBRANES, PK 5
85364 TUBING SET, BUBBLE TRAP QC8000/QC8500
85361 KIT, BUBBLE TRAP, QC8000/QC8500

(The Kit contains the PEEK Bubble trap, 3 membranes, and the tubing and nuts needed for connections)

17.5. MEASURING ORTHO PHOSPHATE UTILIZING TP MANIFOLD

17.5.1. DATA SYSTEM PARAMETERS FOR ORTHO PHOSPHATE

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	45 samples/h, 80 s/sample
Pump Speed:	35
Cycle Period:	80

Analyte Data:

Concentration Units:	µg P/L
Chemistry:	Direct/Bipolar
Expected Inject to Peak Start	21.5 s
Expected Peak Base Width	95 s

Calibration Data:

Level	1	2	3	4	5	6	7
Concentration µg P/L	500	250	100	50	25	10	0

Calibration Fit Type:	1st Order Polynomial
Weighting Method:	1/x
Force through zero:	No

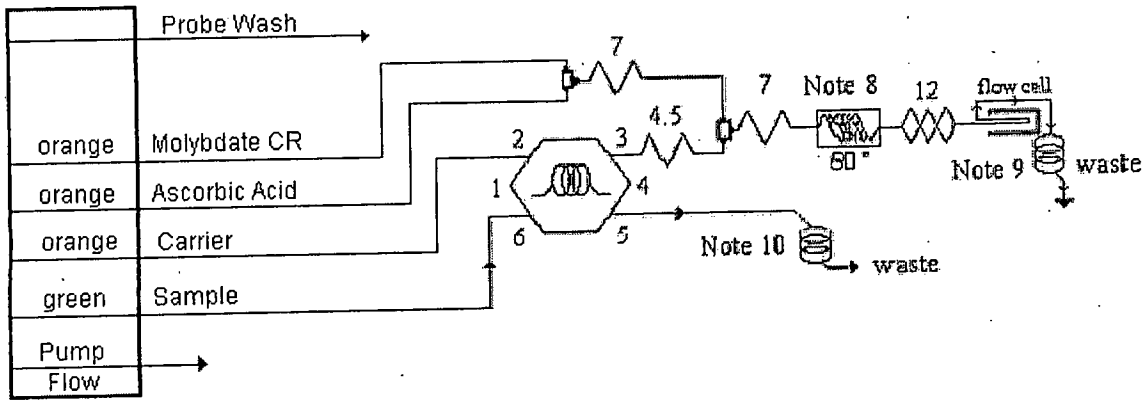
Sampler Timing:

Min. Probe in Wash Period:	5 s
Sample Period:	30 s

Valve Timing:

Load Period:	25 s
Inject Period:	55 s

Ortho Phosphate manifold



Carrier: **DI water**
Manifold Tubing: **0.5mm (0.022 in) i.d.** This is **2.5 µL/cm**.
QC8000/8500 Sample Loop: 200 cm 0.032" i.d.
Interference Filter: 880 nm

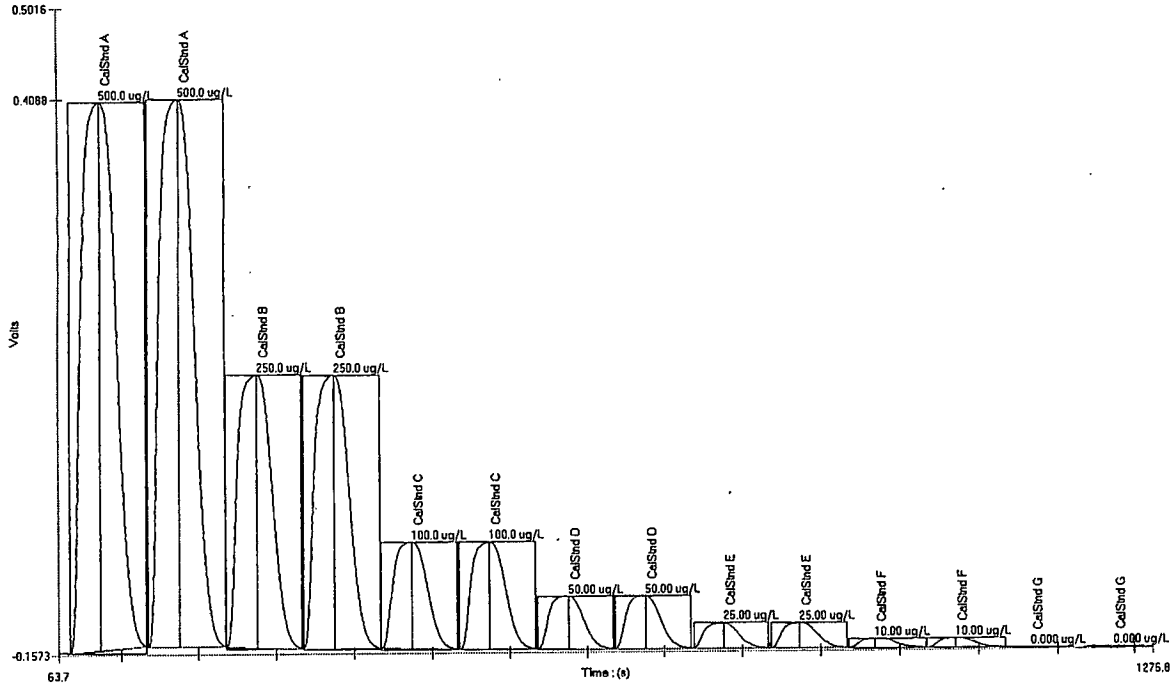
Apparatus: A sample prep module with heater and UV lamp, an injection valve, a 10 mm path length flow cell, a heater  , and a colorimetric detector module are required.

4.5: **70** cm of tubing on a 4.5 cm coil support
7: **135** cm of tubing on a 7 cm coil support
12: **255** cm of tubing on a 12 cm alternating coil support

Note 8: The  shows **175 cm** of 0.8 mm i.d. on the heater is used at the temperature shown.
Note 9: **200 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.
Note 10: The **100 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

When changing the in-line manifold over to run for non-digested Ortho Phosphate, you can remove the debubbler from port 6 of the injection valve to speed up the time to valve time.

Calibration Data for Ortho Phosphate

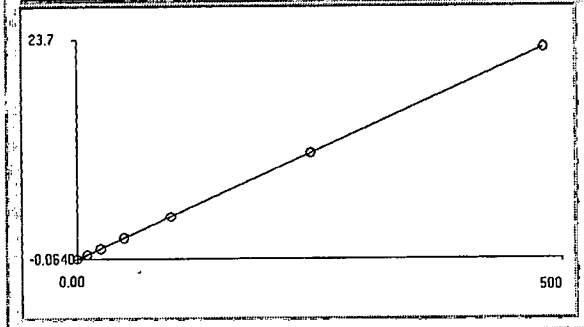


File Name: 12-3 cal support.omn
Acq. Date: 3 Dec 2010

Calibration Graph and Statistics

Calibration Results - Channel 4

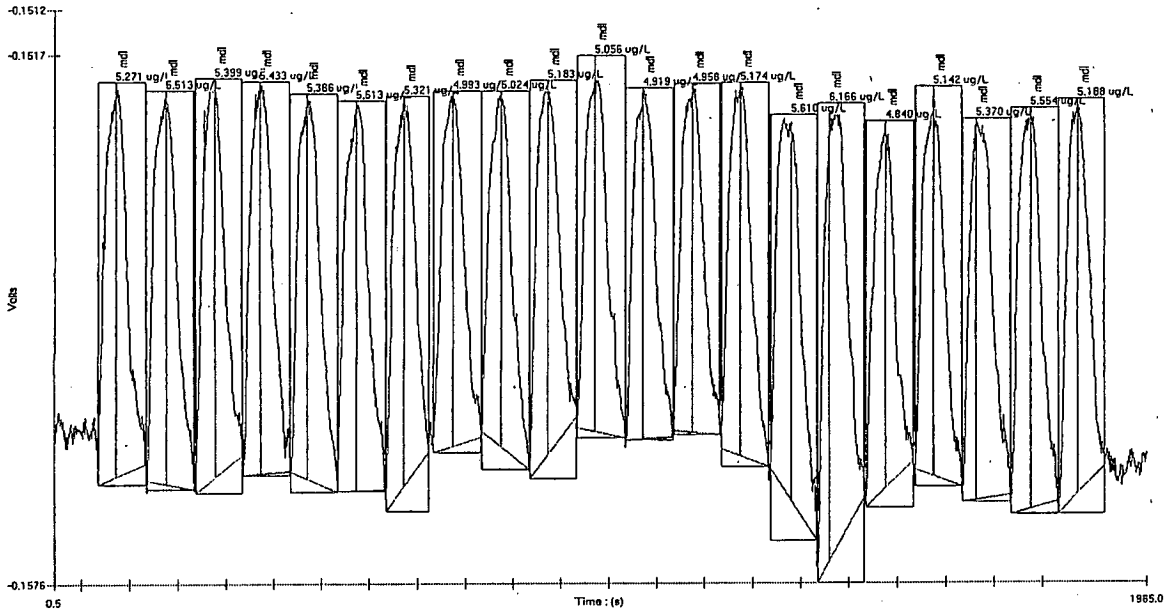
	Known Conc. (ug/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (ug/L)	Date	Time
1	500.0	1	23.70	0.5598	0.2	-0.2	☐	501.1	12/3/2010	7:19:49 AM
2	500.0	2	23.64	0.5585	0.2	9.1e-4	☐	500.0	12/3/2010	7:21:15 AM
3	250.0	1	11.77	0.2786	0.4	0.2	☐	249.5	12/3/2010	7:22:41 AM
4	250.0	2	11.84	0.2797	0.4	-0.4	☐	250.9	12/3/2010	7:24:07 AM
5	100.0	1	4.646	0.1096	0.2	0.8	☐	99.18	12/3/2010	7:25:34 AM
6	100.0	2	4.660	0.1099	0.2	0.5	☐	99.48	12/3/2010	7:27:00 AM
7	50.00	1	2.303	0.05407	0.6	0.5	☐	49.75	12/3/2010	7:28:27 AM
8	50.00	2	2.322	0.05426	0.6	-0.3	☐	50.15	12/3/2010	7:29:53 AM
9	25.00	1	1.115	0.02612	0.2	1.3	☐	24.70	12/3/2010	7:31:20 AM
10	25.00	2	1.118	0.02587	0.2	1.0	☐	24.75	12/3/2010	7:32:47 AM
11	10.00	1	0.4336	0.009550	1.4	-3.6	☐	10.32	12/3/2010	7:34:13 AM
12	10.00	2	0.4248	0.01003	1.4	-1.5	☐	10.14	12/3/2010	7:35:40 AM
13	0.000	1	-0.06399	-0.001650			☐	-0.1773	12/3/2010	7:37:07 AM
14	0.000	2	-0.05280	-0.001478			☐	0.05889	12/3/2010	7:38:35 AM



Area = 0.04740 * Conc - 0.05556
Conc = 21.10 * Area + 1.173
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



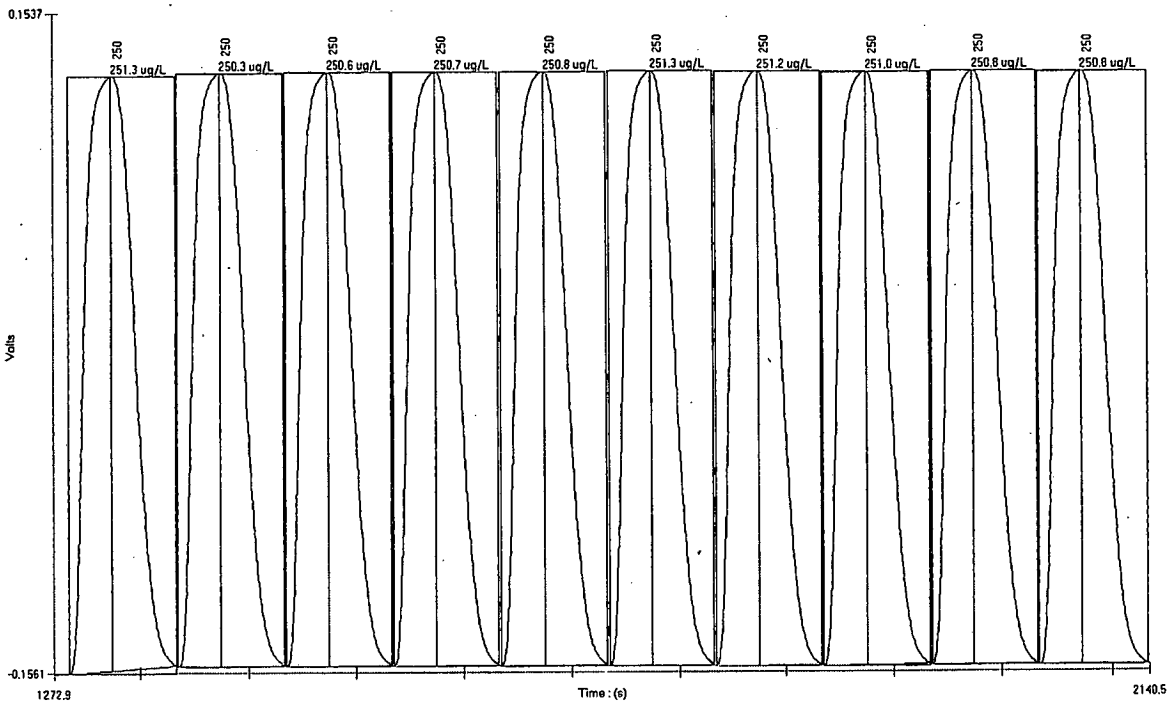
Method Detection Limit for Ortho Phosphate using a 5 µg P/L standard

MDL= 0.776 µg P/L

Standard Deviation (s) = 0.30 µg P/L, Mean (x) = 5.29 µg P/L, Known Value = 5.0 µg P/L

File Name: 12-3 mdl.omn

Acq. Date: 3 Dec 2010



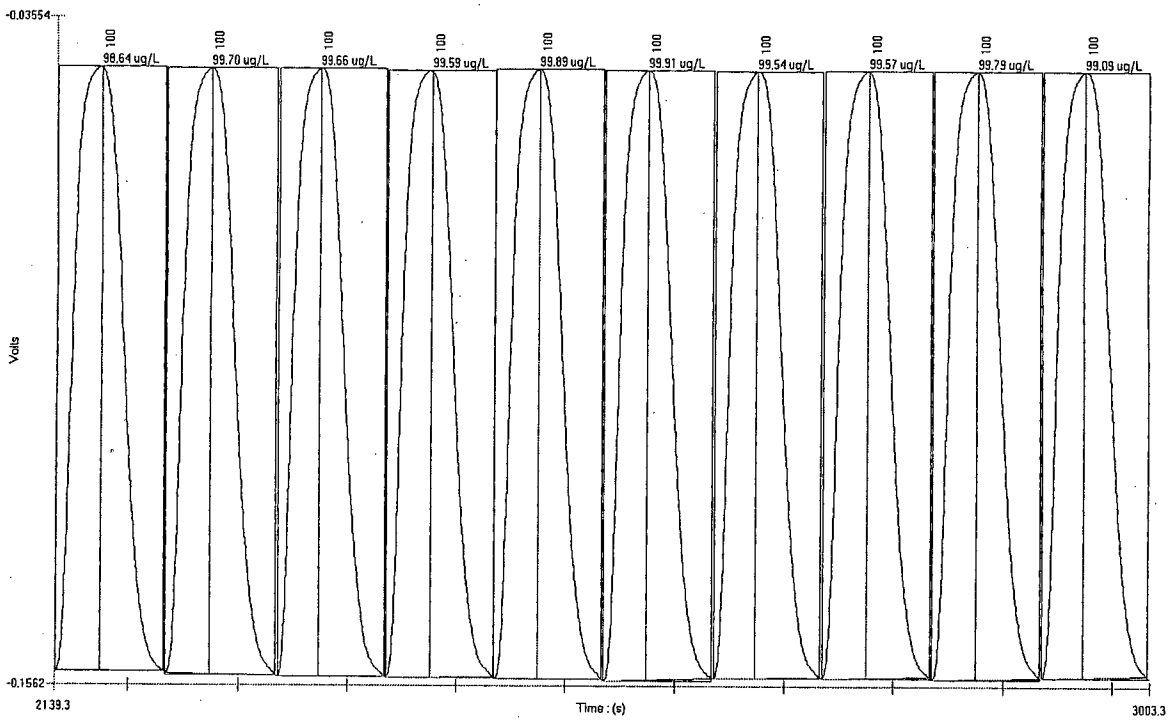
Precision Data for Ortho Phosphate using a 250 µg P/L standard

% RSD =0.128

Standard Deviation (s) = 0.322 µg P/L, Mean (x) = 250.9 µg P/L, Known Value = 250.0 µg P/L

File Name: 12-3 cal support.omn

Acq. Date: 3 Dec 2010



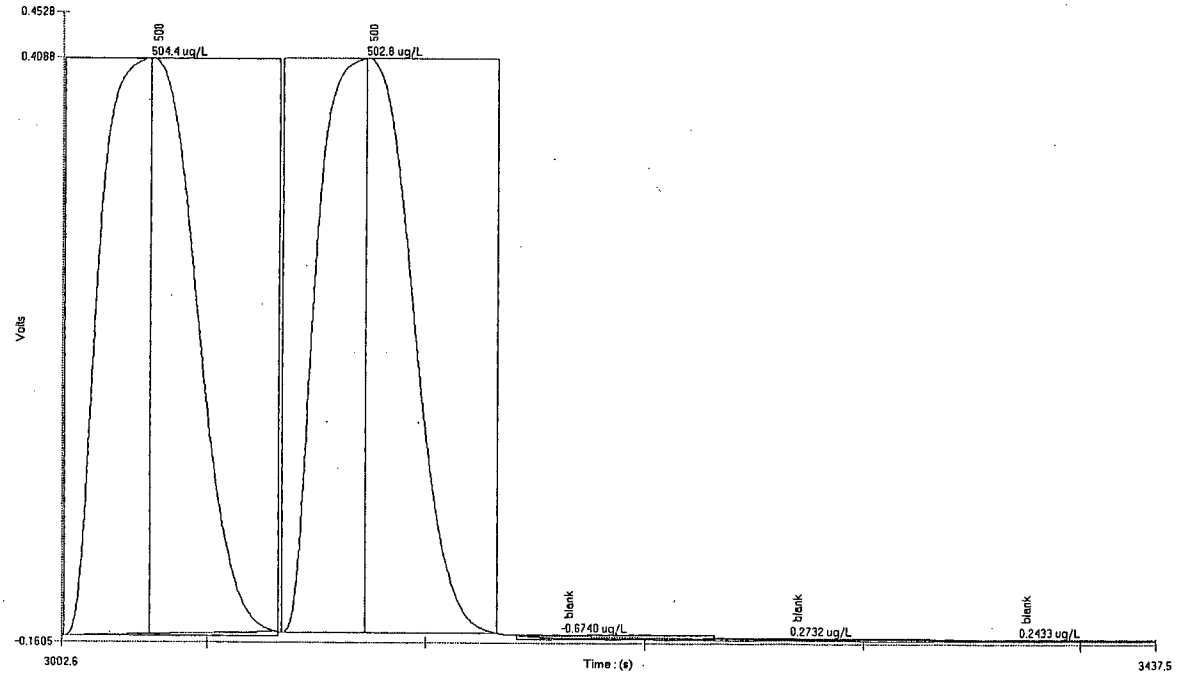
Precision Data for Ortho Phosphate using a 100 µg P/L standard

% RSD =0.393

Standard Deviation (s) = 0.391 µg P/L, Mean (x) = 99.54 µg P/L, Known Value = 100 µg P/L

File Name: 12-3 cal support.omn

Acq. Date: 3 Dec 2010



Carryover Study:

Two 500 µg P/L standards followed by three blanks

Carryover Passed

File Name: 12-3 cal support.omn

Acq. Date: 3 Dec 2010

QuikChem® Method 10-116-29-3-A

DETERMINATION OF DISSOLVED SULFIDE BY FLOW INJECTION ANALYSIS

(In-line distillation)

Written by Ninglan Liao

Applications Group

Revision Date:

4 October 2007

LACHAT INSTRUMENTS
5600 LINDBURGH DRIVE
LOVELAND, CO 80539 USA

LACHAT INSTRUMENTS
A Hach Company Brand

QuikChem® Method 10-116-29-3-A

Dissolved Sulfide, In-line Distillation

0.01 to 2.0 mg S/L

– Principle –

Hydrogen sulfide (H_2S) is released by means of in-line distillation under acidic conditions. The $H_2S_{(g)}$ is separated by a diffusion cell, and then absorbed by a sodium hydroxide solution. The method does not recover sulfide from insoluble matter such as CuS or suspended solids.

The distilled hydrogen sulfide (H_2S) then reacts in acid media and in the presence of ferric chloride with two molecules of N,N-dimethyl-p-phenylenediamine to form methylene blue. The resulting color is read at 660 nm and is proportional to the concentration of H_2S in the sample.

– Interferences –

1. Strong reducing agents at levels of several hundred ppm inhibit color formation.
2. Iodide interferes at levels greater than 2 mg/L.
3. The method is relatively free from interferences because gas dialysis separates the sulfide from sample matrix.
4. During sample collection, sulfide might be lost by oxidation reaction with air or oxidizing agents in sample, such as chlorine. Carefully follow sample collection procedure (Section 6) and analyze the sample immediately after collection.

– Special Apparatus –

Please see Parts and Price list for Ordering Information

1. High temperature heater (Lachat Part No. A85105/A85205)
2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

Revised by S. Tucker October 4, 2007.

CONTENTS

QuikChem® Method 10-116-29-3-A

DETERMINATION OF DISSOLVED SULFIDE WITH INLINE DISTILLATION BY FLOW INJECTION ANALYSIS

1. SCOPE AND APPLICATION

1.1. This method covers the determination of sulfide in drinking, ground, and surface waters, and domestic and industrial wastes.

1.2. The applicable range is 0.01 to 2.00 mg S/L. The statistically determined method detection limit is 0.0007 mg S/L, but 0.006 mg S/L is claimed due to carryover. The method throughput is 15 injections per hour.

2. INTERFERENCES

2.1. Strong reducing agents at levels of several hundred ppm inhibit color formation.

2.2. Iodide interferes at levels greater than 2 mg/L.

2.3. The method is relatively free from interferences because gas dialysis separates the sulfide from sample matrix.

2.4. During sample collection, sulfide might be lost by oxidation reaction with air or oxidizing agents in sample, such as chlorine. Carefully follow sample collection procedure (Section 6) and analyze the sample immediately after collection.

3. SAFETY

3.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

3.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

3.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

3.3.1. Hydrochloric acid

4. EQUIPMENT AND SUPPLIES

4.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

4.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

4.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

4.3.1. Sampler

4.3.2. Multichannel proportioning pump

4.3.3. Reaction unit or manifold

4.3.4. Colorimetric detector

4.3.5. Data system

4.4. Special Apparatus

4.4.1. High temperature heater (Lachat Part No. A85105/A85205)

4.4.2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

5. REAGENTS AND STANDARDS

5.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

Degassing with helium:

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in^2) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

Reagent 1. Hydrochloric Acid, 3 M

By Volume: In a **1 L** volumetric flask containing approximately **600 mL DI water,** slowly add **248 mL concentrated hydrochloric acid** (HCl). Dilute to mark with **DI water** and invert to mix.

By Weight: To a tared **1 L** container, add **752 g DI water** and slowly add **295 g concentrated hydrochloric acid** (HCl). Invert to mix.

Reagent 2. Hydrochloric acid, 0.20 M

By Volume: In a **1 L** volumetric flask, add approximately **700 mL DI water**, then add **16.5 mL concentrated hydrochloric acid** (HCl). Dilute to mark with **DI water** and invert to mix.

By Weight: To a tared **1 L** container, add **983.5 mL DI water**. Then add **19.7 g concentrated hydrochloric acid** (HCl). Invert to mix.

Reagent 3. N,N-Dimethyl-p-phenylenediamine reagent

By Volume: In a **1 L** volumetric flask, dissolve **1.0 g N,N-dimethyl-p-phenylenediamine dihydrochloride** [$(CH_3)_2NC_6H_4NH_2 \cdot 2HCl$], (Aldrich 21,923-1 or equivalent) in about **800 mL 3 M hydrochloric acid solution** (Reagent 1). Dilute to mark with **Reagent 1** and invert to mix. If the prepared reagent appears dark, discard and obtain a fresh supply of the diamine reagent.

Reagent 4. Ferric Chloride, 1.33% (w/v)

By Volume: In a **500 mL** volumetric flask, dissolve **6.65 g ferric chloride hexahydrate** ($FeCl_3 \cdot 6H_2O$) in about **450 mL 0.2 M hydrochloric acid solution** (Reagent 2). Dilute to mark with **Reagent 2** and invert to mix.

Reagent 5. Sodium Hydroxide, 0.025 M (use for standards diluent and carrier)

By Volume: In a **4 L** volumetric flask, dissolve **4 g sodium hydroxide** (NaOH) in approximately **3500 mL DI water.** Dilute to the mark with **DI water** and mix with a magnetic stirrer until dissolved.

By Weight: To a tared **4 L** container, add **4000 mL DI water**, add **4 g sodium hydroxide** (NaOH), and then mix with a magnetic stirrer until dissolved.

Reagent 6. Digestion Solution

In a **1 L** volumetric flask, add approximately **700 mL DI water**, then add **90 mL concentrated phosphoric acid** (H_3PO_4). Dilute to the mark with **DI water**. Mix with a magnetic stirrer and allow the solution to cool. Dilute to the mark after the solution has cooled. Prepare fresh monthly.

5.2. PREPARATION OF STANDARDS

To prepare the stock and working standards, the following containers will be required:

By Volume: One 1 L, one 500 mL, and six 250 mL volumetric flasks.

By Weight: One 1 L, one 500 mL, and six 250 mL containers.

Standard 1. Stock Standard, 100 mg S/L

By Volume: In a **1 L** volumetric flask, dissolve **0.7491 g sodium sulfide nonahydrate** ($Na_2S{\cdot}9H_2O$, Mallinckrodt 8044 or equivalent) in approximately **900 mL 0.025 M sodium hydroxide solution** (Reagent 5). Dilute to the mark with **Reagent 5** and invert to mix. Standardize this solution daily using iodometric titration (see **Standard Methods for the Examination of Water and Wastewater**, 14th Edition, Method 428D, in sources, below).

Standard 2. Working Stock Standard Solution, 10.0 mg S/L

By Volume: In a **500 mL** volumetric flask, add **50.0 mL of Standard 1** (100 mg S/L) and dilute to the mark with **Reagent 5.** Invert to mix.

By Weight: To a tared **500 mL** container, add about **50.0 g Stock Standard 1**. Divide the actual weight of the solution added by 0.1 and make up to this resulting total with **Reagent 5**. Invert to mix.

Working Standards (Prepare Daily)	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
Concentration mg S/L	2.0	1.0	0.5	0.1	0.05	0.02	0.01	0.0

By Volume

Volume (mL) of **standard 2** diluted to 250 mL with **Reagent 5.**	50	25.0	12.5	2.5	1.25	0.5	0.25	---

By Weight

Weight (g) of **standard 2** diluted to final weight (~250 g) divided by **factor** below with **Reagent 5.**	50	25.0	12.5	2.5	1.25	0.5	0.25	---
Division Factor Divide exact weight of the standard by this **factor** to give final weight.	0.2	0.1	0.05	0.01	0.005	0.002	0.001	---

6. SAMPLE COLLECTION, PRESERVATION AND STORAGE

6.1 H_2S in air oxidizes rapidly, so samples and standards should be analyzed without delay. Sulfide also might be lost by oxidation reaction with oxidizing agents in sample, such as chlorine. To eliminate the loss of sample during the sample collection, add 10 drops of 15 M sodium hydroxide (about 0.5 ml) and about 400 mg ascorbic acid into sample container per 100 ml sample first, then add the sample into the container (the sample pH >11). Cool to 4°C and analyze it without delay.

6.2. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

7. PROCEDURE

7.1. INSTALLATION PROCEDURE

7.1.1. The manifold diagram in Section 11.3 has illustrations and detailed instructions for making all fluidic connections. This method employs two sample processing modules (SPM), one SPM for in-line sample distillation and the other SPM for flow injection analysis of the recovered hydrogen sulfide. The SPM for distillation is equipped with a high temperature heater block and diffusion cell, but without the injection valve or the detector. The SPM for sulfide chemistry is equipped with an injection valve, a chemistry manifold, a regular heater block, and a detector.

7.1.2. Place the blank manifold board on top of the SPM for distillation (without valve or detector). As this is done, feed the inlet and outlet tubing from the high temperature heater block upward through the hole of the blank manifold board.

7.1.3. Complete the fluidic connections as described in Section 11.3. Remember to cover the 53 cm outlet line of the high temperature heater in the Distillation SPM with 52 cm of high temperature sleeve (Lachat Part No. 50364) prior to connection with the inlet port of the diffusion cell.

7.2. START UP PROCEDURE

7.2.1. Turn on the system unit and wait for the heater temperature to reach 65°C. Do not pump reagents or water into the flow system until the temperature has reached 65 °C.

7.2.2. After the heater temperature reaches 65°C, pump DI water through all reagent lines and check for leaks and smooth flow. About 20 min is required to reach equilibrium for heater.

7.2.3. Make sure that the sample line pump tube is Red-Red and that the probe wash line is pumping DI water to the probe wash reservoir.

7.2.4. Note that the sample is distilled pre-valve. The sample is initially merged with phosphoric acid and then heated to 65°C. Then the sample is permeated through the diffusion membrane where it is collected in the NaOH stream, and then fed to port 6 of the injection valve. By following the timings in Section 11.1, the pre-valve distillation of sample is taken care of.

7.2.5. If sample concentrations are greater than the high standard, the sample should be diluted with diluent (Reagent 5). When the Dual Resolution diluter is used, Reagent 5 should be used as the diluent. Do not dilute digested samples or standards with DI water.

7.3. CALIBRATION AND DETERMINATION PROCEDURE

7.3.1. Prepare reagent and standards as described in Section 5.

7.3.2. Input data system parameters as in Section 11.1.

7.3.3. Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentration, replicates and QC scheme.

7.3.4. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

7.3.5. After calibration, you can start to analyze the samples.

7.4. SYSTEM MAINTENANCE AND TROUBLESHOOTING PROCEDURE

7.4.1. For information on general system maintenance and troubleshooting, refer to the Troubleshooting Guide in the System Operation Manual. This guide is available on request from Lachat.

7.4.2. In order to get the best results, the system noise needs to be maintained at a low level, such as less than ± 0.0005 volts. In order to eliminate the noise:

a) The tubular membrane debubbler needs to be replaced if air bubble spikes persist. The debubbler lifetime could be one week to one month depending on user maintenance. Follow the shut down procedure (see Section 7.5) to maintain the debubbler.

b) If double peaks or shoulder peak or huge blank peak are observed, the membrane of the diffusion cell needs to be replaced. To prolong the membrane lifetime, run the reagents or DI water through the diffusion cell only at temperature 65°C. Keep the diffusion cell dry after analysis. Follow the start up and shut down procedures (Section 7.2 and 7.5) to maintain the diffusion cell membrane.

7.5. SYSTEM SHUT DOWN PROCEDURE

7.5.1. Put all reagents lines plus the sample probe into DI water. Pump DI water through the manifold for 15 minutes. Keep the heater at 65°C.

7.5.2. Put the distillation line and the sample probe line into an empty container. Pump air through the manifold for 30 minutes to dry the distillation system, especially the membrane. Keep the heater temperature at 65°C while pumping air through the manifold.

7.5.3. Turn off the system unit when the distillation system has dried out.

8. DATA ANALYSIS AND CALCULATIONS

8.1. Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

8.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

8.3. Report results in mg S/L.

9. METHOD PERFORMANCE

9.1. The method support data are presented in section 11. This data was generated according to a Lachat Work Instruction during development of the method.

9.2. Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique, play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

10. REFERENCES

10.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 376.2

10.2. Standard Methods For the Examination of Water and Wastewater, (1998), 20th ed. APHA-AWWA-WPCF, 4500-S, Method D and E, 4-165 to 4-167.

10.3. Chinese Standard Methods, Determination of sulfide – Methylene blue spectrophotometric method, GB/T 16489 - 1996

10.3. D.J. Legget et al., **Anal. Chim. Acta** (1981) 128, 163-168.

10.4. W. Lei and P. Dasgupta, **Anal. Chim. Acta** (1989), 165-170.

11. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

11.1. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000/8500

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	15 samples/h, 240 s/sample
Pump Speed:	35
Cycle Period:	240

Analyte Data:

Concentration Units:	mg S/L
Peak Base Width:	100 s
Inject to Peak Start:	30 s
Chemistry:	Direct

Calibration Data:

Level	1	2	3	4	5	6	7	8
Concentration mg S/L	2.00	1.00	0.50	0.10	0.05	0.02	0.01	0.00

Calibration Rep Handling:	Average
Calibration Fit Type:	2nd Order Polynomial
Weighting Method:	1/X
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	15 s
Probe in Sample Period:	90 s

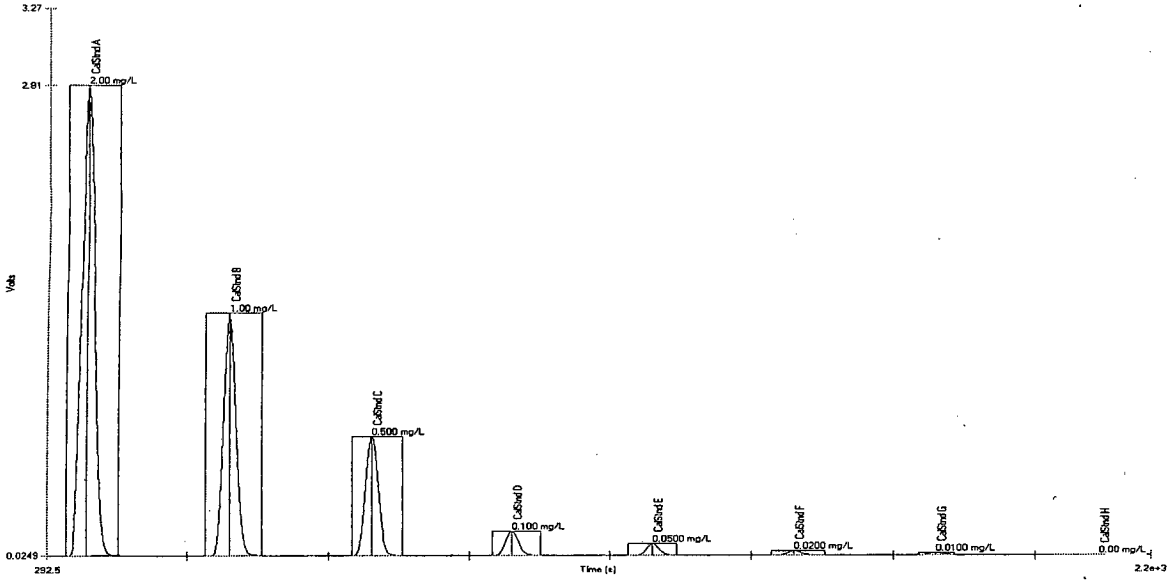
Valve Timing:

Sample reaches first valve:	200 s*
Load Period:	90 s
Inject Period:	150 s

*The time it takes the sample to reach the valve needs to be timed for the specific manifold being utilized. The time listed is just a starting point. The best way to calculate the time to valve is when the sampler probe travels to the sample, it will draw up an air slug. Start timing when the sampler probe goes into the sample, then watch the air slug travel through the heater, then out of the diffusion cell. Once it reaches the debubbler stop timing, and add 5 to 10 seconds for the beginning of the sample slug to reach the valve. This recorded time with the additional 5 to 10 seconds added will be the time that should be entered in the software as the sample reaches first valve.

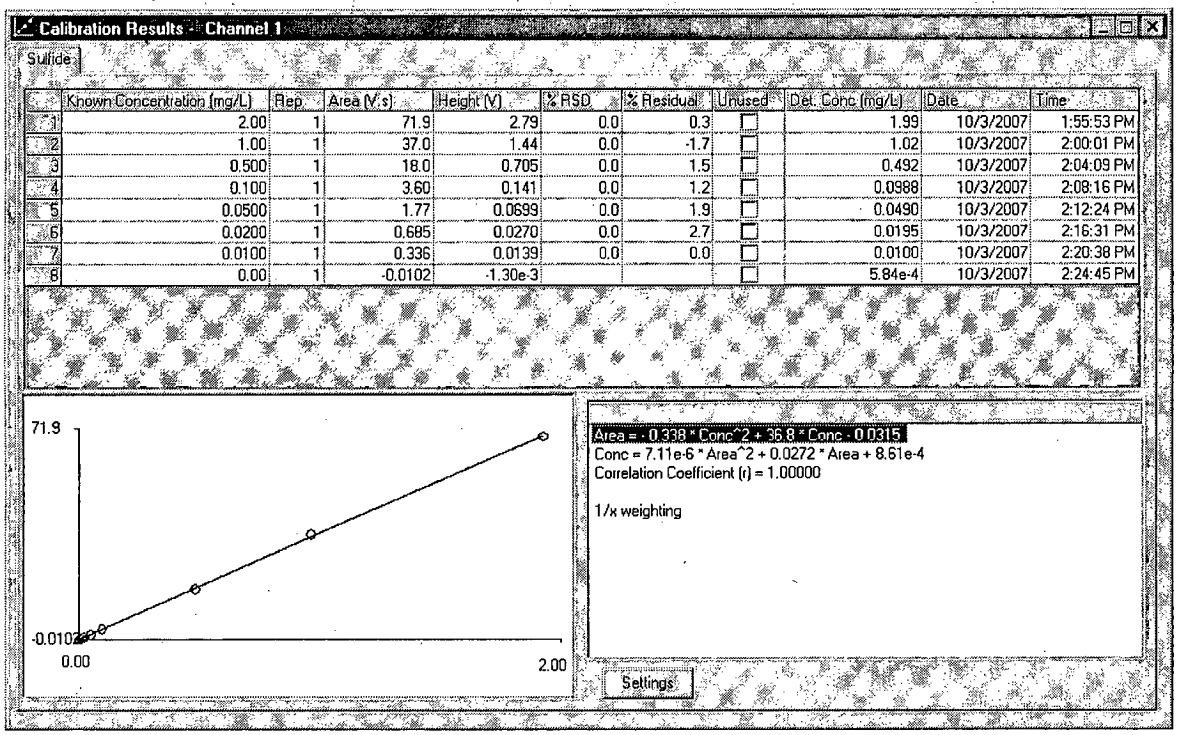
11.2. SUPPORT DATA FOR QUIKCHEM 8000/8500

Calibration Data for Sulfide

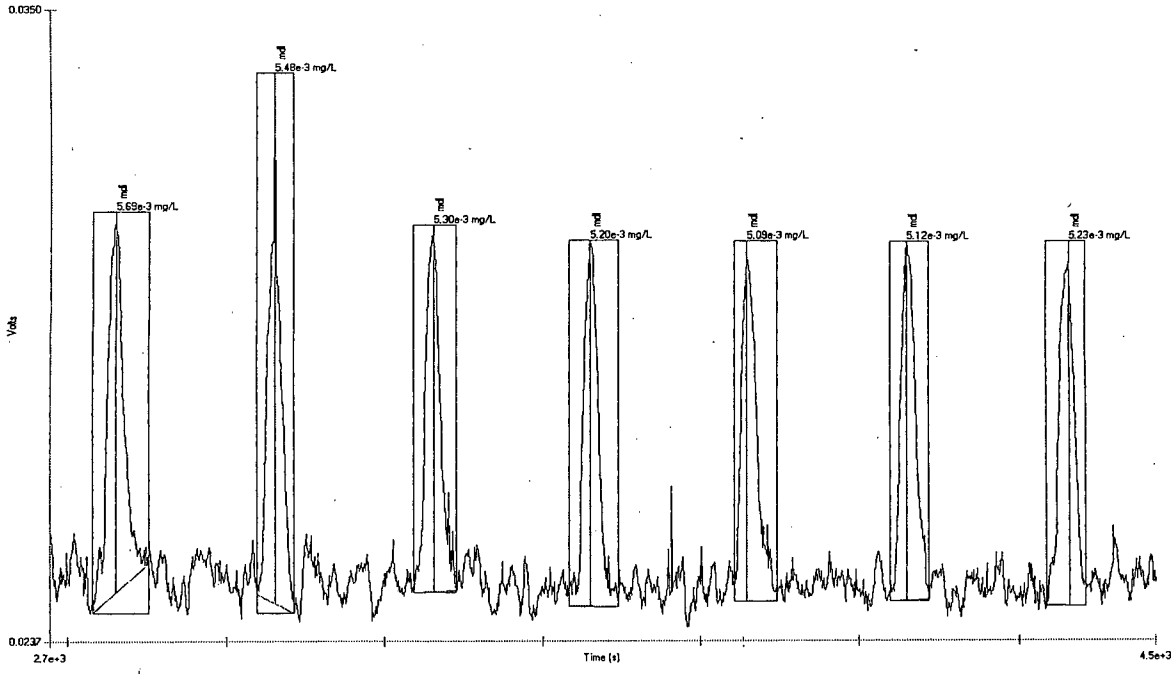


File Name: OM_10-3-2007_01-51-03PM_OMN
Acq. Time: 3 October 2007

Calibration Graph and Statistics



	Known Concentration (mg/L)	Rep	Area (V·s)	Height (V)	% RSD	% Residual	Unused	Det. Conc (mg/L)	Date	Time
1	2.00	1	71.9	2.79	0.0	0.3		1.99	10/3/2007	1:55:53 PM
2	1.00	1	37.0	1.44	0.0	-1.7		1.02	10/3/2007	2:00:01 PM
3	0.500	1	18.0	0.705	0.0	1.5		0.492	10/3/2007	2:04:09 PM
4	0.100	1	3.60	0.141	0.0	1.2		0.0988	10/3/2007	2:08:16 PM
5	0.0500	1	1.77	0.0699	0.0	1.9		0.0490	10/3/2007	2:12:24 PM
6	0.0200	1	0.685	0.0270	0.0	2.7		0.0195	10/3/2007	2:16:31 PM
7	0.0100	1	0.336	0.0139	0.0	0.0		0.0100	10/3/2007	2:20:38 PM
8	0.00	1	-0.0102	-1.30e-3				5.84e-4	10/3/2007	2:24:45 PM



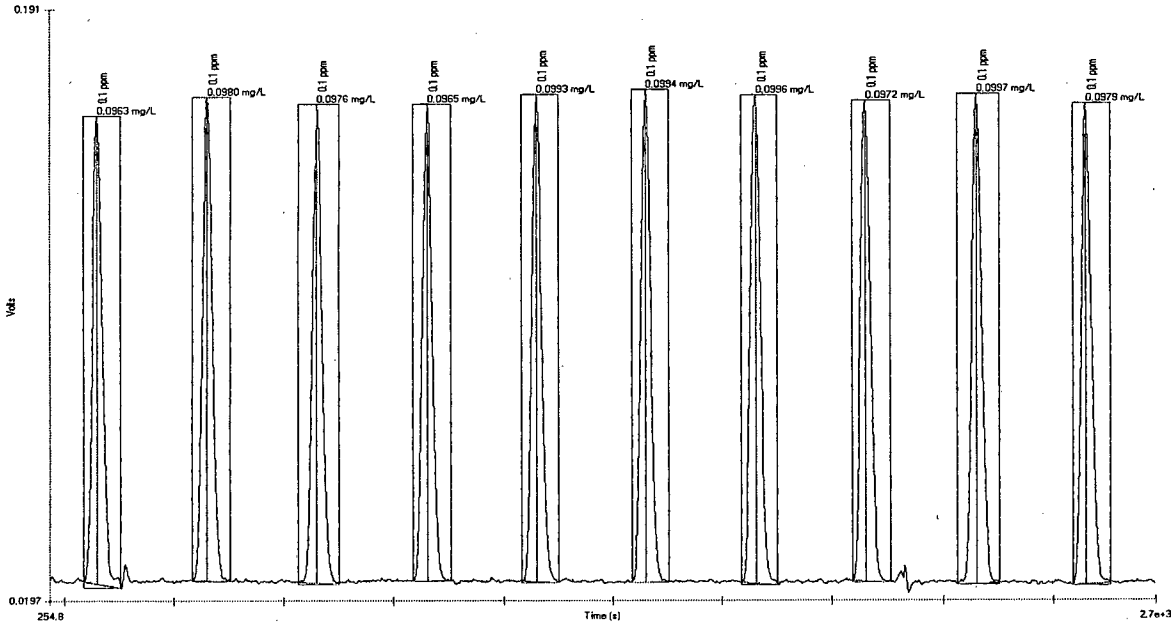
Method Detection Limit for sulfide using a 0.005 mg S/L standard

MDL= 0.0007 mg S/L, claiming 0.006 mg S/L due to carryover

Standard Deviation (s) = 0.0015 mg S/L, Mean (x) = 0.046 mg S/L, Known Value = 0.005 mg S/L

File Name: OM_10-3-2007_02-44-07PM_OMN

Acq. Date: 3 October 2007



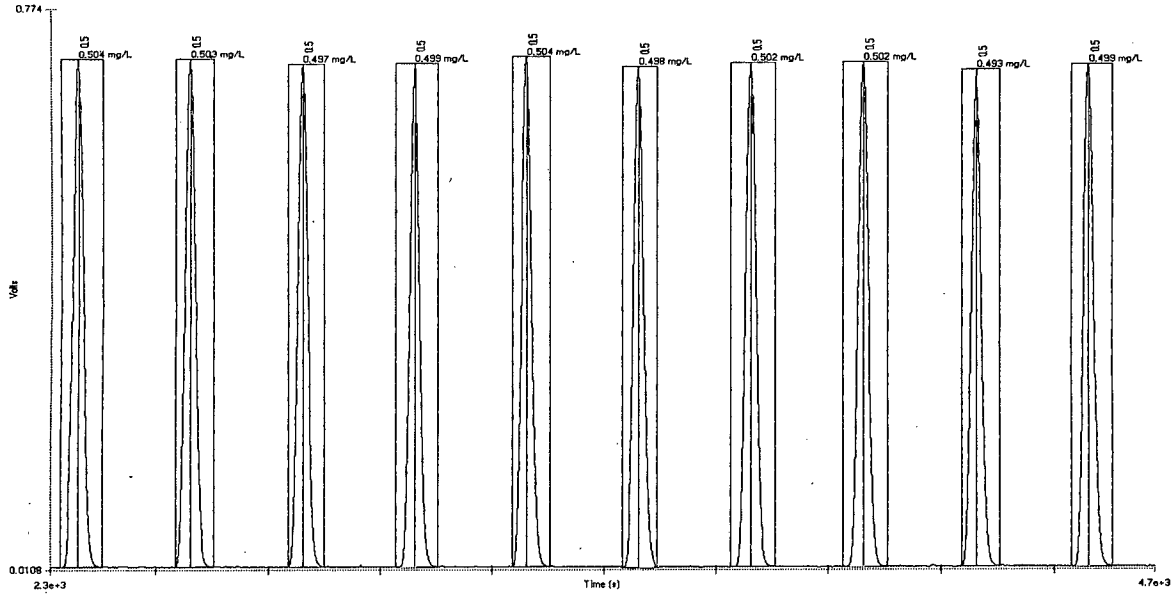
Precision Data for sulfide using a 0.1 mg S/L standard

% RSD =1.3

Standard Deviation (s) = 0.0031 mg S/L, Mean (x) = 0.098 mg S/L, Known Value = 0.1 mg S/L

File Name: OM_10-3-2007_02-44-07PM_OMN

Acq. Date: 3 October 2007



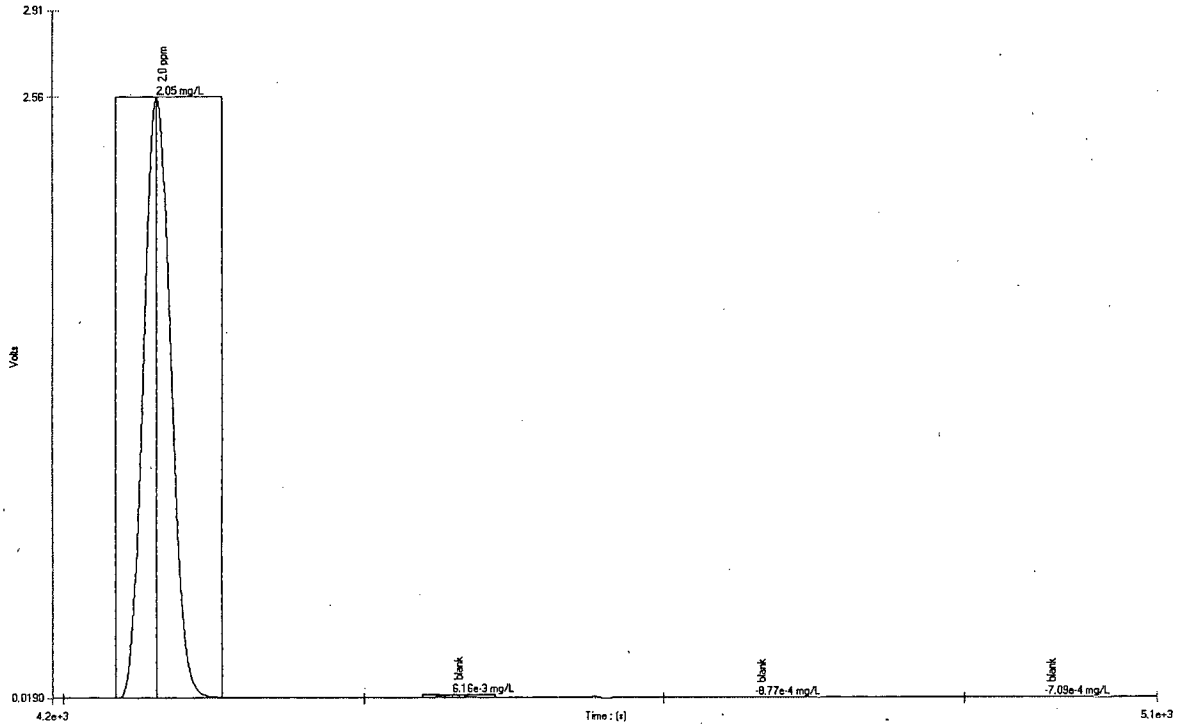
Precision Data for sulfide using a 0.5 mg S/L standard

% RSD =0.71

Standard Deviation (s) = 0.0035 mg S/L, Mean (x) = 0.50 mg S/L, Known Value = 0.5 mg S/L

File Name: OM_10-4-2007_10-11-20AM_OMN

Acq. Date: 4 October 2007

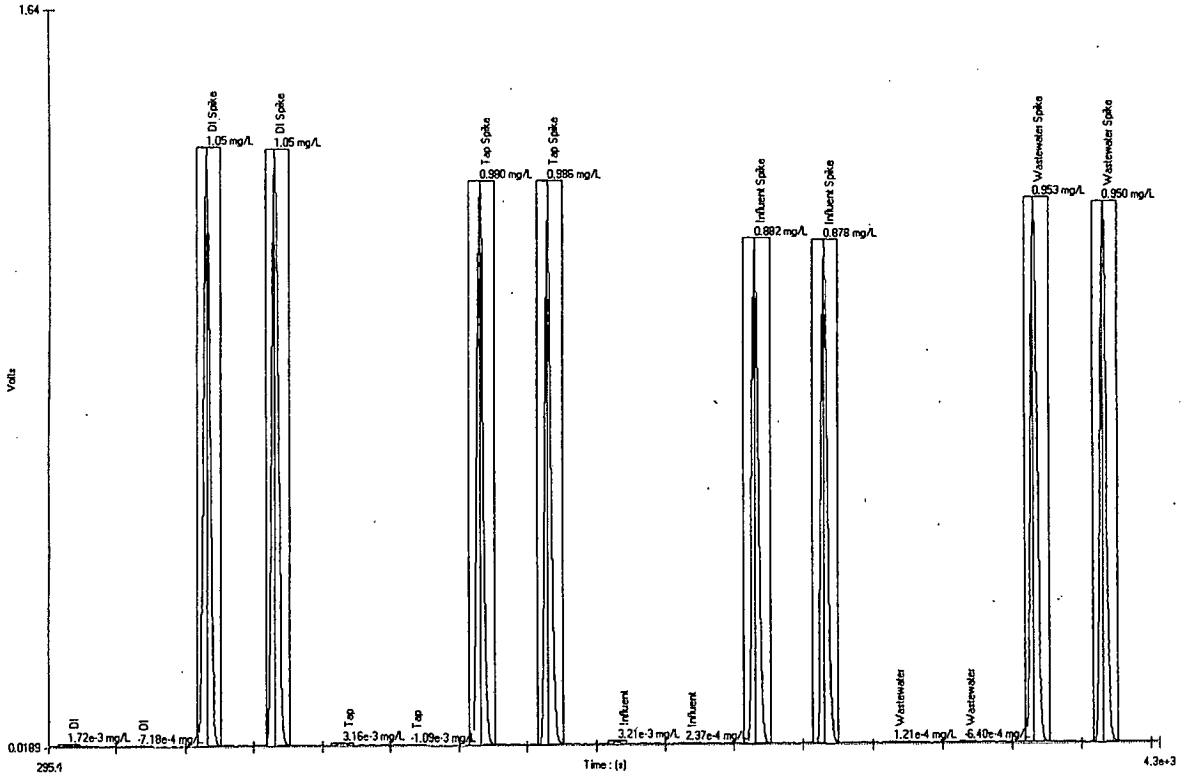


Carryover Study: 2.00 mg S/L standard followed by 3 blanks

Carryover Failed: MDL is reported at 0.006 mg S/L, instead of the statistical calculated value of 0.0007 mg S/L.

File Name: OM_10-5-2007_09-43-29AM_OMN

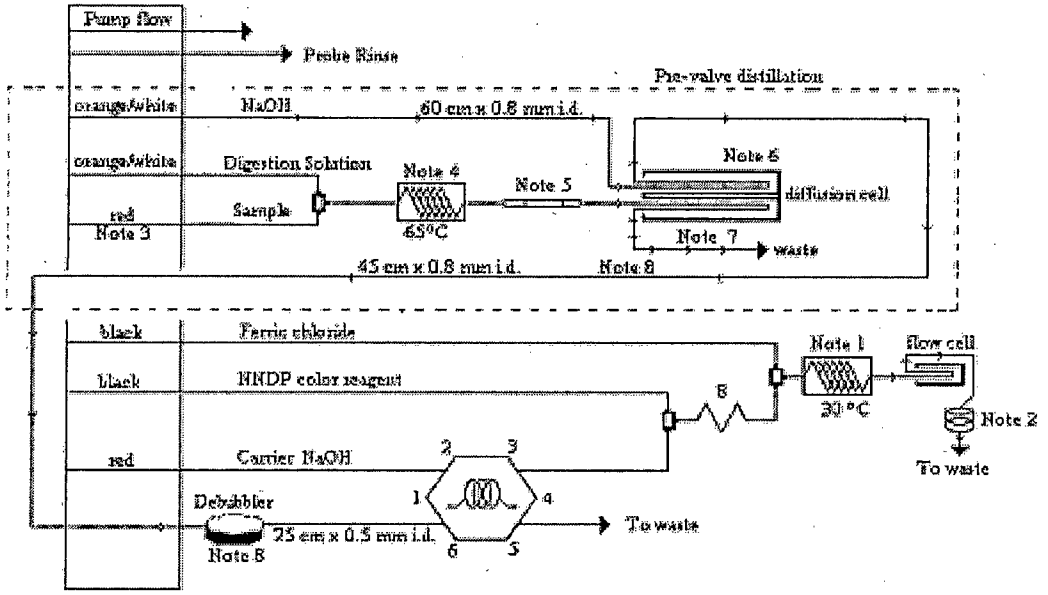
Acq. Date: 5 October 2007



Spike recovery study for sulfide in waters and wastewater matrices.
File Name: OM_10-5-2007_09-43-29AM_OMN
Acq. Date: 5 October 2007

Sample ID	Sample	Results (mg S/L)	Recovery (%)
DI	DI Water	0.0005	---
DI Spike	Spike 1 ppm in DI Water	1.05	105%
Tap	Tap water	0.001	---
Tap Spike	Spiked 1 ppm in Tap water	0.983	98.3%
Influent	Influent Water	0.0017	---
Influent Spike	Spiked 1 ppm in Influent Water	0.880	88.0%
Wastewater	Wastewater	-0.0003	---
Wastewater Spike	Spiked 1 ppm in Wastewater	0.951	95.1%

11.3. SULFIDE MANIFOLD DIAGRAM



Carrier: **0.025 M NaOH** (Reagent 5)
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm**.
AE Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.
QC8000 Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.
Interference Filter: 660 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows tubing wrapped around the heater block at the specified temperature; see manifold notes for the length of tubing used.

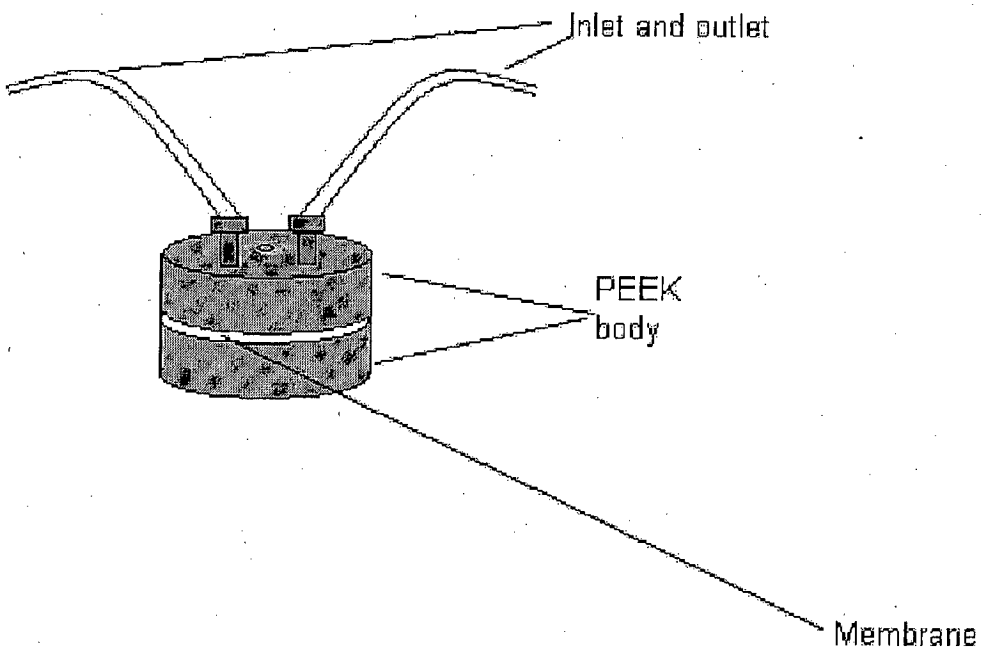
8: **168** cm of tubing on a 8 cm coil support

Note: PVC PUMP TUBES MUST BE USED FOR THIS METHOD
Note 1: 650 cm x 0.8 mm i.d. tubing wrapped on the heater at 30°C
Note 2: 200 cm x 0.5 mm i.d. backpressure loop
Note 3: The sample line is replace with a red/red pump tube. 45 cm x.0.8 mm i.d. is used to connect the sample line to the mixing tee which merges with phosphoric acid.
Note 4: 1200 cm x 0.8 mm i.d. wrapped on the 65°C heater. The lengths of tubing on the heater inlet and outlet are 53 cm.
Note 5: The 53 cm lead of tubing from the outlet of the 65°C heater is covered with 52 cm of high temperature sleeving, (1/16" i.d., Lachat Part No. 50364) for heat insulation and then connected to the diffusion cell inlet on the bottom half.
Note 6: Diffusion cell (Lachat Part No. 50332) is mounted on the manifold board. The Donor (bottom) and Acceptor (top) streams flow in the same direction.
Note 7: To the diffusion cell outlet, bottom half, connect 100 cm x 0.8 mm i.d. manifold tubing plus a waste line (Lachat Part No. 50932)
Note 8: **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of

the debubbler connected to Port 6 of the valve.

Note 9: One o-ring is installed on each of the flares provided with the diffusion cell. Then attach the tan fitting, then a union is attached to each of the flared tubings.

11.4. ALTERNATIVE DEBUBBLER:



This debubbler has holes in the bottom, and a circular membrane sandwiched between two round pices of tan PEEK. Typically, it does not require a backpressure loop on the outlet.

→ When a liquid other than water is passed through this debubbling unit, it is very important that DI water be pumped through it for 5-10 minutes, followed by pumping air for another 5-10 minutes at the end of each days run. This aids in removing salts, acids, and bases that could reduce the lifetime of the membrane, and at least partially dries the hydrophobic membrane material. Membranes typically last 1-3 weeks, or even longer with fastidious care.

If the solution passing through the unit is very hot, it is not unusual to see water droplets on the outside. If bubbles are still entering in the fluid stream but not exiting at the outlet, the unit is still properly functioning despite this condensation.

Membranes are replaced by removal of the Allen screw in the center of the block. The "expired" membrane is removed, and a replacement centered. If the replacement membrane has any text on it, the membrane should be placed so that the text side faces the bottom of the unit.
The part numbers for this are as follows:

85362 BUBBLE TRAP, QC8000/8500 (Not salable)
85363 BUBBLE TRAP, SPARE MEMBRANES, PK 5
85364 TUBING SET, BUBBLE TRAP QC8000/QC8500
85361 KIT, BUBBLE TRAP, QC8000/QC8500

(The Kit contains the PEEK Bubble trap, 3 membranes, and the tubing and nuts needed for connections)

PROCEDURE FOR THE DETERMINATION OF:

ALKALINITY IN WATER BY AUTOMATED TITRATION

Total Alkalinity
Carbonate Alkalinity
Bicarbonate Alkalinity
Carbon Dioxide (free)

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 Alkalinity is a measure of the capacity of a water sample to neutralize an acid and is dependent on the end-point pH that is used in the analysis. Alkalinity, an aggregate measurement, is primarily comprised of hydroxide (OH-), carbonate (CO32-) and bicarbonate (HCO3-) ions. Salts of weak acids such as borates, silicates and phosphates along with salts of some organic acids may also contribute to alkalinity.

1.2 Sources of alkalinity include soils, rocks, salts, industrial wastes and water treatment plants. In receiving streams, alkalinity protects fish and other biota against rapid pH changes associated with accidental spills or discharges. Excess alkalinity, indicating high dissolved salts content, may affect the suitability of water for use in irrigation. Alkalinity acts as a pH buffer in coagulation and lime-soda softening processes in the treatment of potable water. In a wastewater treatment facility, alkalinity levels affect the solids removal processes and in the anaerobic digestion process, the proper alkalinity level needs to be maintained to permit stable nitrification operations.

1.3 This Standard Operating Procedure (SOP) is applicable to the measurement of alkalinity in drinking water, surface water, and groundwater.

1.4 This SOP can be used for sample analysis under the Safe Drinking Water Act (SDWA) and the Clean Water Act.

1.5 The laboratory is certified by the US EPA to use the SOP for sample analysis under the SDWA.

1.6 This SOP is suitable for all concentration ranges of alkalinity. However, appropriate aliquots should be used to avoid a titration volume of greater than 50 mL. The working range is 10 mg/L to 2500 mg/L alkalinity as CaCO3.

1.7 Total alkalinity is measured and reported in standard units of mg/L as CaCO3. Alkalinity may sometimes be reported in milliequivalents (50 mg/L as CaCO3 is equal to 1 milliequivalent/L).

1.8 This SOP is compliant with the requirements of:

Standard Methods, 21st Edition On-line	2320 B
Standard Methods, 21st Edition On-line	4500-CO2 D

2.0 SUMMARY OF METHOD

2.1 An unaltered sample is titrated with 0.02 N H_2SO_4 to an electrometrically determined end-point of pH 4.5. Carbonate alkalinity, bicarbonate alkalinity and carbon dioxide (free) portions of the total alkalinity can be calculated by bicarbonate and carbonate alkalinity spreadsheet from pH and total alkalinity values of the sample. See Section 12 for applicable formulas.

2.2 The sample must not be filtered or concentrated. Dilutions should be avoided if possible.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Method Blank (BLK) immediately before any samples are analyzed and periodically with every group of 20 samples analyzed.

4.2 Substances, such as weak organic and inorganic acids present in large amounts, may cause interference in the electrometric pH measurements.

4.3 Soaps, oily matter, suspended solids, or precipitates can coat the pH electrode, causing sluggish response.

4.4 Since the analysis is pH dependent, samples with a pH at or below 4.5 cannot be analyzed using this method.

4.5 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02.1	Occupational Safety and Health
420.01.1	Right-to-Know

5.3 In addition, the analyst should read the MDH Public Health Laboratory Division – Chemical Hygiene Plan (http://fyi.health.state.mn.us/phl/safety/index.html). Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Health and Safety Officer.

5.4 The analyst should read the Lab Building Emergency Procedures plan (http://fyi.health.state.mn.us/phl/safety/index.html) and know what to do in a variety of emergency situations.

5.5 Safety glasses should be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.6 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.7 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.7.1 Sulfuric Acid

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A.

6.3 Fixed and adjustable pipettes.

6.4 Personal Computer (PC) Titration™ Plus System (Man-Tech Associates, Inc. or equivalent) including:

6.4.1 Autosampler

6.4.2 Millivolt reader

6.4.3 pH electrode

6.4.4 Reagent Rack with Buret I/2

6.4.5 PC Titrate™ Software (version 3.0)

6.4.6 Printer

6.5 Disposable 50 mL conical centrifuge tubes (use once and recycle).

6.6 Disposable transfer pipets.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 megohm-cm at 25°C and free of the analyte phosphorus.

7.2 Only Analytical Reagent (AR) grade or American Chemical Society (ACS) grade chemicals should be used.

7.3 0.02 N H_2SO_4 Titrant: Purchased commercially (JT Baker, Sulfuric Acid, 0.02 N volumetric solution, VWR cat. no. JT5693-20 or equivalent). Stored at room temperature until manufacturer's expiration date.

7.4 Stock Standard 1000 mg/L Alkalinity: In a 1 L volumetric flask, add 1.060 g of Sodium Carbonate (NaCO3) (oven dried at 250°C for 4 hours) to reagent water and dilute to volume. Invert to mix. Store at room temperature for 1 year from preparation date. Storage of the Stock Standard exceeds the length of time allotted in the reference method; the Stock Standard is verified each run by the use of the purchased Second-Source Calibration Verification (SVC). If the SVC does not meet acceptance criteria, prepare a fresh Stock Standard and repeat the run.

7.5 Instrument Performance Check Standard 50 mg/L (ICV): In a 1 L volumetric flask, add 50 mL of Stock Standard 1000 mg/L Alkalinity to reagent water and dilute to volume. Invert to mix. Store at room temperature. Prepare fresh monthly.

7.6 Report Level Verification Standard 10 mg/L (CRL): In a 500 mL volumetric flask, add 5 mL of Stock Standard 1000 mg/L Alkalinity to reagent water and dilute to volume. Invert to mix. Store at room temperature. Prepare fresh monthly.

7.7 Buffer Solution (pH = 4.0): Commercially available (VWR Cat. No. 34170-127 or equivalent). Store at room temperature until manufacturer's expiration date.

7.8 Buffer Solution (pH = 7.0): Commercially available (Ricca Chemical Co., Cat. No. 1551-16 or equivalent). Store at room temperature until manufacturer's expiration date.

7.9 Buffer Solution (pH = 10.0): Commercially available (VWR Cat. No. 34170-133 or equivalent). Store at room temperature until manufacturer's expiration date.

7.10 pH Electrode Filling Solution: Ross Reference Electrode Filling Solution is available commercially (Ross Part No. 810007 or equivalent).

7.11 The Second-Source Calibration Verification (SVC) is a Certified Reference Material from Environmental Resource Associates (or equivalent) that is purchased ready to use. The SVC is stored in a plastic bottle labeled with the date, lot number, and true value, at room temperature.

7.12 All reagents should be discarded if precipitate or growth appears.

7.13 All reagents and standards are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are collected in 2-L, 1-L, or 125-mL plastic bottles and stored at 4°C prior to analysis. Samples should be at room temperature at time of analysis.

8.2 No preservatives should be added to the samples. The alkalinity analyses cannot be performed on acidified samples.

8.3 Maximum holding time is 14 days when stored at 4° ± 2° C.

8.4 Avoid sample agitation and prolonged exposure to air.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability (IDC): The analyst must be able to demonstrate that they can generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial Calibration: The logarithmic calibration range must be determined initially and whenever a significant change in instrument response is observed. The initial calibration must use 3 different pH buffer solutions.

9.1.2 External Verification of Calibration: A Second-Source Calibration Verification (SVC) from an external source is analyzed. The results of the SVC must be within ± 10 % of the established SVC value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limit (MDL) Study: A minimum of 7 replicate Laboratory Control Samples (BS) are spiked at a value 1 to 5 times the estimated detection limit. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated. Once the IDC has been established for this SOP, the Unit Supervisor may waive this requirement for individual analysts if the reference method does not specifically require an MDL study for new analysts.

9.1.4 Initial Precision and Accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.1.6 Demonstration of Low Background: Analyze at least one Method Blank (BLK) to determine reagent or laboratory contamination. The BLK result must meet the criteria established for the on-going demonstration of low background in Section 9.2.3.

9.1.7 Other Requirements for an IDC: An IDC may also be required if there are significant changes to the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis. Consult with the Quality Assurance Officer (QAO) to determine if any changes require an IDC.

9.1.8 IDC Documentation: An IDC for each analyst must be on file in the QA office along with an IDC for the method, matrix, and instrument.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily Calibration: Calibrate the instrument daily with 3 pH buffer solutions. The calibration is accepted if the slope of the curve is between a -54 mV/decade and -60 mV/decade and Calibration Validity prints "True" on the calibration report. Attach printout of curve to data printout.

9.2.2 External Verification of Calibration: Analyze a quality control sample (SCV) from the external source immediately after calibration to verify instrument performance. The results of the SCV must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.3 Demonstration of Low Background: At the beginning of the analytical run, analyze an Initial Calibration Blank (ICB) to determine reagent or laboratory contamination. The background level of the analyte in the ICB must be below the report level (10 mg/L); otherwise the source of the contamination is investigated and corrected before samples are analyzed. With each batch of samples and at the end of the analytical run, analyze a Continuing Calibration Blank (CCB). The value of the CCB must be below the report level for the run to continue. If the CCB is above the report level, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Report Level Verification (LCV) Check: A low report level verification (LCV) check must be performed each time the instrument is calibrated. The LCV check is performed by analyzing a laboratory fortified blank (BS) at or below the report level. The percent recovery of the LCV must be within ± 40%.

9.2.4.1 If the percent recovery of the Report Level Verification standard is outside the acceptance criteria, the analyst must either: 1) repeat the verification check or 2) recalibrate and then perform the Report Level Verification (LCV) check. If the repeat LCV is within acceptance criteria, or if the instrument recalibration results in a Report Level Verification check that is within acceptance criteria, the analyst may proceed with the analytical run. If the second verification check is not within acceptance criteria, the analyst must either: 1) recalibrate the instrument and then perform the Report Level Verification check once again, or 2) perform the LCV at a higher concentration level.

9.2.4.2 If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the report level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed

report level check using the elevated report level until a new calibration curve and report level verification standard meet the acceptance criteria.

9.2.5 Continuing Verification of Calibration: Analyze the Instrument Performance Check (ICV/CCV) sample after calibration. Analyze a CCV after every 10 samples analyzed and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, the ICV/CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.6 Accuracy: There are no fortified blanks or samples with this method; therefore, the ICV/CCV is used to verify accuracy. At the start of an analytical run, analyze the ICV/CCV. Accuracy (as percent recovery) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Found Concentration of ICV/CCV}}{\text{True Concentration of ICV/CCV}} \times 100$$

9.2.7 If the recovery of the analyte falls outside the required control limits of 90-110%, the analyte is judged out of control. The source of the problem should be identified and the situation resolved before sample analysis can continue.

9.2.8 Precision: Analyze a laboratory duplicate (DUP) with each batch of field samples processed as a group, or 10% of the field samples analyzed, whichever is greater. Calculations of the absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.8.1 Calculate the relative percent difference of the duplicates using the following formula:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = concentration of sample

D = concentration of duplicate sample

9.2.8.2 Duplicate acceptance criteria:

Concentration Range	Criteria:
RL to 10xRL	None
10xRL to highest calibration std	RPD ≤ 10%

9.2.8.3 If the duplicate concentration is between the RL and 10xRL, and the RPD is greater than 10%, the qualifier QH is added to the duplicate: "RPD between sample duplicates not within acceptance limits. Analyte concentration in the samples too low for proper evaluation."

9.2.8.4 If the duplicate fails to meet the above criteria, the samples should be reanalyzed to verify poor duplicate analysis RPD. If the repeated duplicate is still not within acceptable limits, the samples must be reported with a qualifier identifying the sample analysis result as yielding poor duplicate analysis RPD.

9.3 External verification of laboratory performance: Proficiency Test (PT) samples are analyzed as required for Federal certification. If the results are not within acceptance criteria, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance Officer.

9.4 The MDL study is repeated when changes in instrumentation or instrument response occur. A minimum of 7 replicate Laboratory Control Samples (LCS) are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3) MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of BLK, SVC, LCV, ICV, and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 3 pH buffer solutions for calibration (see Section 7.7 – 7. 9).

10.2 Process pH buffer solutions as described in Section 11.

10.3 Purchased titrant comes standardized.

10.4 Prepare calibration curve by plotting instrument response against concentration values. A calibration curve is fitted to the calibration standard concentration/response data by the PC Titrate™ software (version 3.0). Slope is acceptable if calibration validity prints "True" on the calibration report. Make a copy of the curve to document the initial calibration.

10.5 After the calibration has been established, it must be verified by the analysis of a Method Blank (BLK), a suitable quality control sample (SVC) an instrument performance check (ICV/CCV), a report level verification (LCV) and a continuing calibration blank (CCB).

10.5.1 The background level of the analyte in the BLK or ICB/CCB must be below the report level (10 mg/L); otherwise the source of the contamination is investigated and corrected before samples are analyzed.

10.5.2 The results of the LCV must be within ± 40% of the true value (10 mg/L) in order to proceed. If it is not, follow the procedure outlined in Section 9.2.4.

10.5.3 If measurements exceed ± 10% of the established ICV or SVC value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.4 A CCV and a CCB must be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 10 mg/L. The results for the CCV must be within ± 10% of the true value (50 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

10.6 Print the calibration statistics when calibration is complete. The PC Titrate™ software should do this automatically.

11.0 PROCEDURE

11.1 System start-up:

11.1.1 Fill rinse water jug with reagent water.

11.1.2 Fill reagent bottle with 0.02 N H_2SO_4.

11.1.3 Drain pH electrode using a disposable transfer pipet. Rinse 1-2 times with a small amount of electrode filling solution, then fill electrode with filling solution.

11.1.4 Turn on computer and double click on the PC Titrate™ for Windows Icon and log-in.

11.2 Calibration:

11.2.1 Select "Run Titration" from the Titrator menu. Click on the load template box and select "ALKALINITY INITIAL QC" from template list.

11.2.2 Pour 35 mL of each pH buffer solution into 50 mL centrifuge tubes and place in ascending order in the sample tray of the autosampler. Follow the software template to place the initial QC set in the sample tray. The initial QC set includes: reagent water (purge), BLK, SVC, ICV, LCV and

CCB. The last position on the last sample tray is reserved for a rinse with reagent water. For the initial QC set and end rinse, pour 35 mL of each into 50 mL centrifuge tubes and place in order on the tray.

11.2.3 Click "START" to begin. The system will ask if you want to purge entire buret, click [YES]; next it will ask you to fill electrodes, click [OK].

11.2.4 The calibration and initial QC will automatically print out at the end.

11.2.5 Verify calibration as described in Sections 10.4 and 10.5.

11.3 Sample Analysis:

11.3.1 Click on the load template box and select "ALKALINITY SAMPLES" from the template list. Download the sample numbers. After sample numbers and QC samples are entered, click [CHECK Timetable]. Fix any errors in the timetable, making sure no two samples have the same sample number.

11.3.2 The CCVs and CCBs should be placed after every 10 samples and at the end of the run. Laboratory duplicates should be set up for every 10 samples. An analytical batch consists of 10 samples or less.

11.3.3 Pour 35 mL of samples, CCV's and CCB's into 50 mL centrifuge tubes and place them into the corresponding spot in the autosampler tray. The last spot on the autosampler tray is reserved for the electrode storage solution (30 mL of pH 4 buffer solution and 5 mL of the Fluoride Stock Standard).

11.3.4 Click [START] to begin.

11.3.5 Once the run begins, use [PRIORITY] if you need to pause the run. Do not click on [STOP] because this will terminate the run. Once it finishes the sample it is presently running, you will be able to return to the template and add samples to the run or make any changes needed. Hit [RESUME] to continue with the run.

11.4 System Shut-down:

11.4.1 The PC Titrate™ system can be safely left to run overnight and it needs no special shut down procedure.

11.4.2 The sample results will automatically print out when it is complete.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations are performed by the PC Titrate™ software system. The pH buffers are used to calibrate the pH probe by creating a curve between the potentiometric measurements of the electrode versus the concentrations of the buffers. The software calculates the slope, intercept and correlation for the curve. The software uses this information to measure the pH in the samples during the titration to an endpoint of pH 4.5 where it calculates the amount of acid added to the sample to use in determining the value for alkalinity.

12.2 The method detection limit (MDL) is calculated as described in Section 9.1.3. The current MDL value is on file in the QA Office.

12.3 The minimum report level is 10.0 mg/L as $CaCO_3$.

12.4 Results are reported in mg/L as $CaCO_3$ to two significant figures.

12.5 Sample results and quality control data from the sample run are transferred electronically to Element after review by the analyst.

12.6 The original concentration of any laboratory duplicate analysis is reported.

12.7 Bicarbonate alkalinity and carbonate alkalinity are calculated using the pH and total alkalinity results. This calculation is performed in the Bicarbonate and Carbonate Alkalinity Calculation spreadsheet (Appendices I) and entered into LIMS. The following formulas are from Standard Methods, 21th Ed. Method 4500-CO_2-D.

12.7.1 Bicarbonate alkalinity (HCO_3^- mg/L as $CaCO_3$) calculation:

$$\text{Bicarbonate alkalinity} = \frac{\text{Total alkalinity(mg } CaCO_3\text{/L)} \; - \; 5\times10^{(\text{pH} \; - \; 10)}}{1 \; + \; 0.94\times10^{(\text{pH} \; - \; 10)}}$$

12.7.2 Carbonate alkalinity (CO_3^{2-} mg/L as $CaCO_3$) calculation:

$$\text{Carbonate alkalinity} = 0.94 \times \text{Bicarbonate alkalinity} \times 10^{(\text{pH} \; - \; 10)}$$

12.8 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1 Information pertinent to our laboratory's performance is available in the QA Office.

13.2 Current MDL data are available in the QA Office.

13.3 Precision and accuracy data are available in the QA Office.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult, "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C., 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reduction, reclamation, recycling.

- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 All waste from this method can be flushed down the drain. For additional information regarding the laboratory's waste management policy, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

16.0 BIBLIOGRAPHY

16.1 Standard Methods for the Examination of Water and Wastewater. Method 2320 B, pp. 2-27, and 4500-CO_2 D, pp.4-34. 21st Edition On-line.

16.2 "Methods for Chemical Analysis of Water and Wastes." U.S. Environmental Protection Agency, Method 310.1, 1983.

16.3 "Appendix B to Part 136-Definition and Procedure for the Determination of Method Detection Limit-Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

16.4 "Annual Book of ASTM Standards", Vol. 11.0, Method D1067-92, 1996.

17.0 TABLES, FIGURES, VALIDATION DATA

17.1 The Initial Demonstration of Capability data are on file in the QA Office; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

Approved By: /s/Jeffrey Brenner Date: 10/12/2011
Jeffrey Brenner, Inorganic Unit Supervisor

Approved By: /s/ Paul Moyer Date: 10/12/2011
Paul Moyer, Environmental Lab Section Manager

APPENDIX I

Bicarbonate and Carbonate Alkalinity Calculations

Minnesota Department of Health
Public Health Laboratory

Promium Samples	Total Alkalinity Result (mg/L)	pH	Bicarbonate Alkalinity (mg/L)	Carbonate Alkalinity (mg/L)	Date of Calculation	Batch
11I0372-01	488.5994	7.567	486.9	1.7	10/7/11 13:54	B1J0136
11I0372-02	491.2967	7.714	488.9	2.4	10/7/11 13:54	B1J0136
11I0374-01	481.1416	7.632	479.2	1.9	10/7/11 13:54	B1J0136
11I0382-01	484.6756	7.611	482.8	1.9	10/7/11 13:54	B1J0136
11I0581-01	414.2968	7.445	413.2	1.1	10/7/11 13:54	B1J0136
11I0581-02	416.3823	7.443	415.3	1.1	10/7/11 13:54	B1J0136
11I0582-01	418.3195	7.468	417.2	1.2	10/7/11 13:54	B1J0136
11I0653-01	235.5337	7.607	234.6	0.9	10/7/11 13:54	B1J0136
11I0655-01	236.1746	7.621	235.2	0.9	10/7/11 13:54	B1J0136
11I0657-01	300.5269	7.66	299.2	1.3	10/7/11 13:54	B1J0136
11I0660-01	309.8412	7.803	308.0	1.8	10/7/11 13:54	B1J0136
11I0661-01	251.2309	7.488	250.5	0.7	10/7/11 13:54	B1J0136
11I0740-01	38.66475	9.972	18.1	15.9	10/7/11 13:54	B1J0136
11I0741-01	205.6209	7.7	204.6	1.0	10/7/11 13:54	B1J0136
11I0752-01	363.1365	7.823	360.8	2.3	10/7/11 13:54	B1J0136
11I0752-02	362.0576	7.869	359.5	2.5	10/7/11 13:54	B1J0136
11I0755-01	387.0221	7.497	385.9	1.1	10/7/11 13:54	B1J0136
11I0758-01	344.0957	7.637	342.7	1.4	10/7/11 13:54	B1J0136
11I0760-01	347.1638	7.522	346.1	1.1	10/7/11 13:54	B1J0136
11I0762-01	316.7536	7.902	314.4	2.4	10/7/11 13:54	B1J0136
11I0762-02	277.7798	7.794	276.1	1.6	10/7/11 13:54	B1J0136
11I0765-01	323.55	7.961	320.7	2.8	10/7/11 13:54	B1J0136
11I0766-01	336.6613	7.471	335.7	0.9	10/7/11 13:54	B1J0136
11I0769-01	239.1038	7.831	237.6	1.5	10/7/11 13:54	B1J0136
11I0771-01	327.1535	7.51	326.1	1.0	10/7/11 13:54	B1J0136
11I0774-01	269.2214	7.519	268.4	0.8	10/7/11 13:54	B1J0136
11I0776-01	267.5586	7.61	266.5	1.0	10/7/11 13:54	B1J0136
11I0778-01	247.0127	7.696	245.8	1.1	10/7/11 13:54	B1J0136
11I0778-02	290.2895	7.646	289.1	1.2	10/7/11 13:54	B1J0136
11I0778-03	283.4137	7.541	282.5	0.9	10/7/11 13:54	B1J0136
11I0780-01	325.9748	7.529	324.9	1.0	10/7/11 13:54	B1J0136
11I0780-02	288.5461	7.604	287.4	1.1	10/7/11 13:54	B1J0136
11I0780-03	309.3765	7.658	308.0	1.3	10/7/11 13:54	B1J0136
11I0780-04	283.4826	7.593	282.4	1.0	10/7/11 13:54	B1J0136
11I0790-01	253.6584	7.653	252.6	1.1	10/7/11 13:54	B1J0136
11I0790-02	236.6131	7.719	235.4	1.2	10/7/11 13:54	B1J0136
11I0790-03	255.6329	7.723	254.3	1.3	10/7/11 13:54	B1J0136
11I0790-04	277.0632	7.473	276.3	0.8	10/7/11 13:54	B1J0136

gen001 Bicarbonate and Carbonate Calculation Form
rev1, revised 10-10-2011

Calculations Verified 10-10-2011

PROCEDURE FOR THE DETERMINATION OF:

AMMONIA IN WATER
BY
FLOW INJECTION ANALYSIS COLORIMETRY

Total Ammonia Nitrogen
Dissolved Ammonia Nitrogen

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 Ammonia is present naturally in surface water and wastewater. Its concentration generally is low in groundwater because it absorbs to soil particles and clay and is not leached readily from soils. It is produced largely by deamination of organic nitrogen-containing compounds and by hydrolysis of urea. At some water treatment plants, ammonia is added to react with chlorine to form a combined chlorine residual. In the chlorination of wastewater effluents containing ammonia, virtually no free residual chlorine is obtained until the ammonia has been oxidized. Rather, the chlorine reacts with ammonia to form mono- and dichloramines.

1.2 This Standard Operating Procedure (SOP) is applicable to the measurement of ammonia in drinking, ground, and surface waters.

1.3 This SOP can be used for sample analysis under the Clean Water Act (CWA).

1.4 The working range is 0.05 to 5.0 mg/L. Dilutions are prepared for concentrations greater than 5.0 mg/L. The working range of the reference method is 0.01 to 2.0 mg/L.

1.5 Unpreserved samples for dissolved ammonia are filtered through a 0.45 µm membrane filter at the time of collection or when received by the laboratory.

1.6 This SOP is compliant with the requirements of EPA 350.1 using the Lachet QuikChem® Method 10-107-106-1-C. Approval letters (Appendices I and II).

1.6.1 The manifold in this SOP is from the 2 November 2001 revision of QuikChem® Method 10-107-106-1-C.

2.0 SUMMARY OF METHOD

2.1 The method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction product is measured at 630 nm, and is directly proportional to the original ammonia concentration.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Method Blank (BLK) with each batch of no more than 20 samples.

4.2 Cyanate, which may be encountered in certain industrial effluents, will hydrolyze to some extent even at the pH of 9.5 at which distillation is carried out.

4.3 Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate or other reagents before distillation.

4.4 Calcium and magnesium ions may precipitate if present in sufficient concentrations. Tartrate or EDTA is added to the sample in-line in order to prevent this problem.

4.5 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02.1	Occupational Safety and Health
420.01.1	Right-to-Know

5.3 In addition, the analyst should read the MDH Public Health Laboratory Division – Chemical Hygiene Plan (http://fyi.health.state.mn.us/phl/safety/index.html). Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Health and Safety Officer.

5.4 The analyst should read the Lab Building Emergency Procedures plan (http://fyi.health.state.mn.us/phl/safety/index.html) and know what to do in a variety of emergency situations.

5.5 Safety glasses should be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.6 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.7 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.7.1 Hydrochloric Acid

5.7.2 Phenol

5.7.3 Sodium Nitroferricyanide

5.7.4 Sodium Hydroxide

5.7.5 Sulfuric Acid

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance – Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A. All non disposable glassware must be rinsed with 1:1 Hydrochloric acid (HCl) followed by three rinses with reagent water prior to use.

6.3 Fixed and adjustable pipettes.

6.4 Flow injection analysis equipment designed to deliver and mix samples and reagents in the required order and ratios (Lachat Instrument or equivalent).

6.4.1 Autosampler

6.4.2 Multichannel proportioning pump

6.4.3 Reaction unit or manifold

6.4.4 Colorimetric detector

6.4.4.1 Flow Cell: 10 nm, 80 µL.

6.4.4.2 Interference Filter: 630 nm.

6.4.5 Omnion® software (version 3.0)

6.4.6 Printer

6.4.7 Lachat Special Apparatus

6.4.8 Heating Unit

6.4.9 PVC pump tubing must be used for this SOP.

6.5 Disposable 13X100 mm test tubes (use once and discard).

6.6 Vortex mixer.

6.7 Pall Gelman IC Acrodisc 0.45µm syringe filters (PN4485) are used for dissolved ammonia nitrogen analysis. These filters have a certified background level for filter extractables of less than 1 ppb for ammonia and require no pretreatment.

6.8 pH paper to check samples at time of receipt for proper preservation.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 megaohm-cm at 25°C and free of the analyte ammonia.

7.2 Only Analytical Reagent (AR) grade or American Chemical Society (ACS) grade chemicals should be used.

7.3 Degassing with Helium: To help prevent bubble formation, reagents may be degassed. Use 20 lb/in^2 through a helium degassing wand. Bubble He through the solution for at least 10 minutes.

7.4 Sodium Phenolate Reagent: In an acid-rinsed, 500 mL volumetric flask, add 400 mL of degassed (if necessary) reagent water, 44 mL of 88% of liquefied phenol, and 16 g of sodium hydroxide (NaOH). Stir until dissolved. Dilute to 500 mL with reagent water. Prepare fresh daily.

7.5 Sodium Hypochlorite Reagent: Purchase through available vendor. 2-3% (w/w) sodium hypochlorite (NaOCl), ready to use. Use manufacturer's expiration date.

7.6 Buffer Reagent: In an acid-rinsed, 1-L volumetric flask, dissolve 50.0 g disodium ethylenediamine tetraacetate dihydrate ($Na_2EDTA \cdot 2H_2O$) and 9.0 g sodium hydroxide (NaOH) in approximately 900 mL reagent water. Stir until dissolved. Dilute to mark with reagent water. Prepare fresh daily. Degas if necessary.

7.7 Sodium Nitroprusside Reagent: In an acid-rinsed, 500 mL volumetric flask, dissolve 1.75 g of sodium nitroprusside (sodium nitroferricyanide $[Na_2Fe(CN)_5NO \cdot 2H_2O]$) in degassed (if necessary) reagent water. Dilute to volume and invert to mix. Prepare fresh daily.

7.8 Carrier Reagent: In an acid-rinsed 1 L volumetric flask, add approximately 900 mL reagent water. Then add 2 mL concentrated sulfuric acid (H_2SO_4) or 20 mL 10% sulfuric acid (H_2SO_4). Dilute to volume and invert to mix. Prepare fresh daily. Degas if necessary.

7.9 Calibration Standards:

7.9.1 Stock Standard (1000 mg/L): In an acid-rinsed, 1 L volumetric flask, dissolve 3.819 g ammonium chloride (NH_4Cl) (dried for at least two hours at 110°C) in about 800 mL reagent water. Dilute to the mark and invert to mix. Remake yearly.

7.9.2 Intermediate Stock Standard #1 (100 mg/L): In an acid-rinsed 100 mL volumetric flask, add 10 mL of the 1000 mg/L ammonia stock standard solution and 2 mL of 10% sulfuric acid (H_2SO_4) to approximately 80 mL reagent water. Dilute to the mark with reagent water and invert to mix. Prepare fresh daily.

7.9.3 Intermediate Stock Standard #2 (10 mg/L): In an acid-rinsed, 100 mL volumetric flask, add 10 mL of the Intermediate Stock Standard Solution #1 (100 mg/L) and 2 mL of 10% sulfuric acid (H_2SO_4) to approximately 80 mL reagent water. Dilute to the mark with reagent water and invert to mix. Prepare fresh daily.

7.9.4 Working Calibration Standards: To prepare 100 mL quantities of calibration standards, use acid-rinsed, 100 mL volumetric flasks. Use the table below to put the correct amount and type of stock standard in

each volumetric flask. Then add 2 mL of 10% sulfuric acid (H_2SO_4). Dilute to the mark with reagent water and invert to mix.

Calibration Standard	Quantity of 10 mg/L Intermediate Stock Standard (#2)	Quantity of 100 mg/L Intermediate Stock Standard (#1)
0.05 mg/L	500 µL	—
0.10 mg/L	1.0 mL	—
0.50 mg/L	—	500 µL
1.0 mg/L	—	1.0 mL
2.5 mg/L	—	2.5 mL
5.0 mg/L	—	5.0 mL

Prepare daily.

7.9.5 Calibration blank and diluent: In an acid-rinsed, 500 mL volumetric flask, add approximately 400 mL of reagent water and 10 mL of 10% sulfuric acid. Dilute to the mark and invert to mix.

7.10 The second-source calibration verification (SCV) is purchased and prepared according to instructions provided by the manufacturer. The prepared SCV is stored in a plastic bottle labeled with the date, lot number, true value, and is stored at 4° C ± 2 ° C.

7.11 1:1 Hydrochloric Acid: Add an equal volume of concentrated HCl (37%) to reagent water. This reagent is prepared by designated laboratory personnel and used to acid rinse glassware.

7.12 0.5 N H_2SO_4: In an acid-rinsed, 500-mL volumetric flask, add 50 mL of 5 N H_2SO_4 and dilute to volume with reagent water.

7.13 All reagents should be discarded if precipitate or growth appears.

7.14 All reagents and standard are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are collected in 125 mL or 250 mL plastic bottles and stored at 4°C ± 2°C prior to analysis.

8.2 Samples are preserved at the time of collection by the addition of 2 mL 10% H_2SO_4 per 100 mL of sample. For a 125 mL bottle, add 2.5 mL 10% H_2SO_4. For a 250 mL bottle, add 5 mL H_2SO_4.

8.3 When the sample is received in the laboratory, a pH check is done with pH paper to verify that the sample has been preserved properly. Record this preservative check in the computer. If pH is not ≤ 2, the sample is acidified with nutrient preservative (10% H_2SO_4) and the qualifier PC: "Preservation completed in laboratory" entered into the LIMS.

8.4 If dissolved analysis is requested and the sample has not been filtered in the field, the samples must be filtered upon arrival. Filter sample into a 250 mL plastic nutrient bottle, preserve with 10% H_2SO_4 (use 2 mL preservative for every 100 mL of filtrate) and store at 4°C ± 2°C prior to analysis. Preserved samples for ammonia cannot be filtered for dissolved analysis. One filter blank should be run for each batch of twenty samples that are filtered.

8.5 Maximum holding time is 28 days when stored at 4°C ± 2°C.

9.0 QUALITY CONTROL

1.1 Initial Demonstration of Capability (IDC): The analyst must be able to demonstrate that they can generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial Calibration: The 1st order calibration range must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument.

9.1.2 External Verification of Calibration: A second-source calibration verification standard (SCV) from an external source is analyzed. The results of the SCV must be within ± 10 % of the established SCV

value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limit (MDL) Study: A minimum of 7 replicate laboratory Control Samples (BS) are spiked at a value 1 to 5 times the estimated detection limit and processed over a period of three days. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated. Once the IDC has been established for this SOP, the Unit Supervisor may waive this requirement for individual analysts if the reference method does not specifically require an MDL study for new analysts.

9.1.4 Initial Precision and Accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.1.6 Demonstration of Low Background: Analyze at least one Method Blank (BLK) to determine reagent or laboratory contamination. The BLK result must meet the criteria established for the on-going demonstration of low background in Section 9.2.3.

9.1.7 Other Requirements for an IDC: An IDC may also be required if there are significant changes to the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis. Consult with the Quality Assurance Officer (QAO) to determine if any changes require an IDC.

9.1.8 IDC Documentation: An IDC for each analyst must be on file in the QA office along with an IDC for the method, matrix, and instrument.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily Calibration: Calibrate the instrument at the beginning of the analytical run or whenever the curve verification fails. Calibrate the instrument with a calibration blank and at least 3 calibration standards covering the range of sample results and within the Linear Calibration Range (LCR) of the analyte. The curve used must be linear and not forced through zero. Acceptable correlation coefficient for the calibration curve is 0.9990 or greater. The concentration of the calibration standards must be ± 10% of the true value, and ± 20% of the true value for the lowest standard. This corresponds to the percent residual calculation. The Calibration Statistics display on the analysis report summarizes in algebraic form what is seen graphically. The first equation shows the plotted calibration equation in the form of **Area f (Conc.)**, where the peak area is a function of **Conc.** or determined concentration of the analyte. The second equation is the same calibration equation, but solved for concentration. It is in the form **CONC = f (Area)**. This is the equation that is used to determine the concentration of unknowns. The third statistic is the value of **r**, the 'correlation coefficient' for the calibration.

9.2.2 External Verification of Calibration: Analyze a second-source calibration verification (SCV) from the external source immediately after calibration to verify instrument performance. The results of the SCV must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples. If the SCV is out of control, the run data can only be accepted by the Unit Supervisor.

9.2.3 Demonstration of Low Background: At the beginning of each run and with each batch, analyze an initial calibration blank (ICB) or blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK or ICB must be below the report level; otherwise the source of the contamination is investigated and corrected before samples are analyzed. Analyze a continuing calibration blank (CCB) every 10 samples and at the end of the run. The CCB must be less than the report level (MRL). If the CCB is above the Report Level, the source of the deviation is investigated and corrected before

the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Report Level Verification (RLV) Check: A Report Level Verification (CRL) check must be performed each time the instrument is calibrated. The CRL check is performed by analyzing a calibration standard at or below the report level (0.05 mg/L). (The CRL check sample is not required to be processed through the entire SOP.) The percent recovery of the CRL must be within ± 40%.

9.2.4.1 If the percent recovery of the CRL is outside the acceptance criteria, the analyst must either: 1) repeat the CRL or 2) recalibrate and then perform the CRL. If the repeat CRL is within acceptance criteria, or if the instrument recalibration results in a CRL that is within acceptance criteria, the analyst may proceed with the analytical run. If the CRL is not within acceptance criteria, the analyst must either: 1) recalibrate the instrument and then perform the CRL once again, or 2) perform the CRL at a higher concentration level.

9.2.4.2 If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the Report Level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed CRL using the elevated Report Level until a new calibration curve and CRL meet the acceptance criteria.

9.2.5 Continuing Verification of Calibration: Analyze a continuing calibration verification standard (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.6 Accuracy: With every batch of 20 samples processed as a group, analyze a laboratory control sample (BS). Accuracy (as percent recovery) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Found Concentration of BS}}{\text{True Concentration of BS}} \times 100$$

9.2.7 If the recovery of the analyte falls outside the required control limits of 90-110%, the analyte is judged out of control. The source of the problem should be identified and the situation resolved before sample analysis can continue.

9.2.8 Matrix Effect: Run a matrix spike (MS) with each batch of 20 field samples processed as a group, or 5% of the samples analyzed, whichever is greater. The same solution used to fortify the BS is used to fortify the MS. Accuracy (as percent recovery after background correction) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Concentration of MS - Concentration of Matrix Sample}}{\text{True Concentration of MS}} \times 100$$

9.2.9 If the recovery of the MS falls outside of 90-110% limits, the MS is repeated. If the recovery of the repeat analysis also falls outside the control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the analyte still falls outside the designated MS recovery range and the BS, and ICV/CCV for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be matrix induced and the results for the diluted sample and the MS are reported using an elevated report level reflective of the dilution used and the qualifier QD: "Recovery in MS not within acceptance limits" is added to the MS.

9.2.7.1 If the MS recovery of the diluted sample is within acceptable limits, the sample is reported with an elevated Report Level reflective of the dilution used.

9.2.10 Precision: Analyze a laboratory duplicate (DUP) with each batch of field samples processed as a group, or10% of the field samples analyzed, whichever is greater. Calculations of the absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.10.1 Calculate the relative percent difference of the duplicates using the following formula:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = concentration of sample

D = concentration of duplicate sample

9.2.10.2 Duplicate acceptance criteria:

Concentration Range	Criteria:
RL to 10xRL	None
10xRL to highest calibration std	RPD ≤ 10%

9.2.10.3 If the duplicate concentration is between the RL and 10xRL, and the RPD is greater than 10%, the qualifier QH is added to the duplicate: "RPD between sample duplicates not within acceptance limits. Analyte concentration in the samples too low for proper evaluation."

9.2.10.4 If the duplicate fails to meet the above criteria, the samples should be reanalyzed to verify poor duplicate analysis RPD. If the repeated duplicate is still not within acceptable limits, the samples must be reported with a qualifier identifying the sample analysis result as yielding poor duplicate analysis RPD.

9.3 External verification of laboratory performance: Proficiency Test (PT) samples are analyzed as required for Federal certification. If the results are not within acceptance criteria, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance Officer.

9.4 The MDL study is repeated when changes in instrumentation or instrument response occur. A minimum of 7 replicate Laboratory Fortified Blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3) MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Dissolved Analysis: The filtration blank results must be below the Report Level. If the filter blank is above the Report Level, consult with a lead worker or supervisor to determine if the filter blank result should be subtracted from the sample results or if other action should be taken.

9.6 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of ICV, ICB, SCV, CRL, CCV and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 6 calibration standards and a calibration blank by diluting suitable volumes of calibration standard solution, as described in Section 7.9.

10.2 Set up the manifold as shown in Section 17. If necessary, refer to the Lachat manual for instrument operation.

10.3 Process calibration standards and calibration blank and calibrate the instrument as described in Section 11. Read calibration standards and calibration blank in descending concentration on the Lachat.

10.4 Prepare calibration standard curve by plotting instrument response against concentration value. The curve used must be linear and not forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the Omnion® 3.0 Software. Attach a pdf of the curve to the sequence in Element to document the initial calibration. The calibration standard curve is accepted if a correlation coefficient of at least 0.9990 is achieved. Also the concentration of the standards must be within ± 10% of their true value except the lowest standard which can be ± 20% of its true value.

10.5 After the calibration has been established, it must be verified by the analysis of the ICV, ICB, SCV, CRL, CCV and CCB.

10.5.1 If measurements exceed ± 10% of the established ICV value (1.0 mg/L), the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.2 The background level of the analyte in the ICB must be at or below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed.

10.5.3 The results of the CRL must be within ± 40% of the true value (0.05 mg/L) in order to proceed. If it is not, follow the procedure outlined in Section 9.2.4.

10.5.4 If measurements exceed ± 10% of the established SCV value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.5 A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) must be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 0.05 mg/L. The results for the calibration verification standard (CCV) must be within ± 10% of the true value (1.0 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the

instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

11.0 PROCEDURE

11.1 System Start-up

11.1.1 Prepare reagents and standards as described in Section 7.

11.1.2 Set up manifold as shown in Section 17.2 and inspect manifold for proper connections.

11.1.3 Turn on power strip. Allow at least 15 minutes for the heating unit to warm up to 60°C.

11.1.4 Raise tension levers on pump tube cassettes. Place reagent lines into reagent water and check for leaks and smooth flow. Allow water to pump for a few minutes.

11.1.5 Transfer lines to designated reagent. Place lines into reagents in this order: Carrier, Buffer, Phenolate, Hypochlorite, and Nitroprusside. This is done to reduce staining of the manifold tubing. Allow system to equilibrate until a stable baseline is achieved.

11.2 Prepare a BS or MS by adding 50 µL of Intermediate Stock Standard #1 (100 mg/L) into a 10 mL borosilicate test tube. Add 5.0 mL reagent water or field sample. The true value is 1.0 mg/L.

11.3 Prepare a CRL by using the lowest non-zero standard, 0.05 mg/L. Pour 5 mL of the 0.05 mg/L standard into a 10 mL borosilicate test tube.

11.4 Calibration and Sample Analysis

11.4.1 Prepare standards as described in Section 7.

11.4.2 Place calibration standards in descending order in the auto sampler standards tray. Select the default Ammonia template from the Ammonia data folder and input the information required by the data system, such as concentration, replicates, and QC scheme. Verify peak timing and integration parameters as specified in Section 17.3. Import the sequence ID numbers from Element Database.

11.4.3 Pour approximately 5 mL of each type of quality control sample into a 10 mL borosilicate test tube and place in sample tray.

11.4.4 The CCV and CCB must be set up every 10 samples and at the end of each run in the template. The CCV is the 1.0 mg/L calibration standard. The CCB is the same as the calibration blank. The CCV and CCB come from the same cup as the equivalent calibration standard. Input the information required for the QC scheme. See Section 17.

11.4.5 Pour approximately 5 mL of each sample, filter blank, or sample aliquot diluted to 5 mL, into corresponding 10 mL borosilicate test tubes and place in sample tray. Set up 1 DUP for every 10 samples, and a BS and MS every 20 samples.

11.4.6 Calibrate the instrument by injecting standards. The data system will then associate the concentrations with the instrument responses for each standard and evaluate the curve.

11.4.7 After acceptable curve is achieved and initial QC is obtained and acceptable, continue with analysis.

11.5 System Shut Down

11.5.1 At the end of the run place all reagent lines into water to rinse. If any tubing on the manifold appears stained, pump 10% hydrochloric acid solution to remove the staining. It is important that the acid is dilute. Place these lines in reagent water and pump for an additional five minutes. Then pump all lines dry.

11.5.2 Turn off the pump and the power strip. Release the tension levers on the pump tube cassettes.

11.6 System and Procedure Notes

11.6.1 For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual (Guide is also available on request from Lachat). Consult the Instrument Book for the Lachat systems for current information on preventative maintenance procedures.

11.6.2 Samples that are over concentrated should be diluted with the diluent and not reagent water.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calibration is accomplished by injection of standards. The data system will then prepare a calibration curve by plotting instrument response versus standard concentration. Sample concentration is calculated from the regression equation. Multiply results by appropriate dilution factor.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file in the QA Office.

12.3 The minimum report level is 0.05 mg/L.

12.4 Results are reported in mg/L to three significant figures.

12.5 Sample results and quality control data are transferred electronically to the Element Database for review by the analyst.

12.6 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 5.0 mg/L are diluted and reanalyzed.

12.7 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1 Information pertinent to our laboratory's performance is available in the QA Office.

13.2 Current MDL data are available in the QA Office.

13.3 Precision and accuracy data are available in the QA Office.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult, "Less is Better: Laboratory Chemical Management to Waste

Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C., 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reduction, reclamation, recycling.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 Sodium nitroprusside and sodium phenolate are considered hazardous. Collect all waste containing these reagents. They are collected in suitable waste storage

containers labeled "hazardous waste" and disposed of by the Hazardous Waste Specialist.

15.3 For additional information regarding the laboratory's waste management policy, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

16.0 BIBLIOGRAPHY

16.1 "Methods for Chemical Analysis of Water and Wastes." U.S. Environmental Protection Agency, Method 350.1, Revision 2.0, August 1993.

16.2 Standard Methods for the Examination of Water and Wastewater. Method 4500-NH3 H. 21st Edition, On-line.

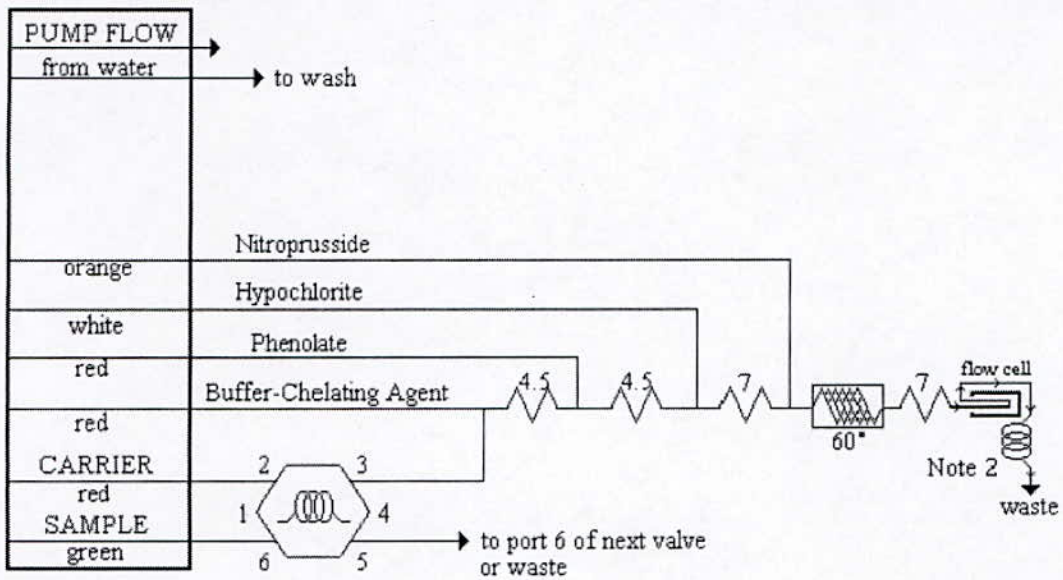
16.3 "Appendix B to Part 136-Definition and Procedure for the Determination of Method Detection Limit-Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

16.4 Lachat Instruments QuikChem® Method 10-107-06-1-C, Determination of Ammonia in Waters by Flow Injection Analysis Colorimetry.

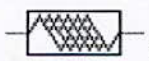
17.0 TABLES, FIGURES, VALIDATION DATA

17.1 The Initial Demonstration of Capability data are on file in the QA Office; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

17.2 Ammonia Manifold Diagram:



QC 8000 Sample Loop: 75 cm of 0.8 mm id tubing.
Interference Filter: 630 nm
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2µL/cm.
Apparatus: An injection, a 10 mm path length flow cell, and a colorimetric detector module are required.

 : 650 cm of 0.8 mm tubing wrapped around the heater block set at 60° C.
Carrier: Section 7.8.
4.5: 70 cm of 0.8 mm tubing on a 4.5 cm coil support.
7: 135 cm of tubing on a 7 cm coil support.

Note 1: PVC pump tubing must be used for this method.
Note 2: 200 cm x 0.22 in i.d. backpressure loop.

17.3 Quik Chem® 8000

17.3.1 The timing values listed below are approximate and may need to be optimized using graphical events programming.

Sample throughput: 60 samples/hour, 60 seconds/sample
Pump speed: 35
Cycle speed: 60

17.3.2 Analyte Data:

Concentration Units: mg/L of NH_3 N
Expected Inject to Peak Start: 20 seconds
Expected Peak Base Width: 49 seconds
Chemistry: Direct

17.3.3 Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg/L N	5.00	2.50	1.00	0.50	0.10	0.05	0.0

Calibration Fit Type: 1st Order Polynomial
Calibration Rep. Handling: Average
Weighting Method: None
Force through Zero: No

17.3.4 Sampler Timing

Min. Probe in Wash Period: 5 seconds
Sample Period: 24 seconds

17.3.5 Valve Timing

Load Period: 15 seconds
Inject Period: 45 seconds
Time to Valve: 26 seconds

Approved By: /s/ Jeffrey Brenner Date: 11-15-2011
Jeffrey Brenner, Inorganic Unit Supervisor

Approved By: /s/ Paul Moyer Date: 11-15-2011
Paul Moyer, Environmental Lab Section Manager

Appendix I

NPDES Equivalent Methods Do NOT Require Letter From USEPA

Lachat Instruments has received many questions regarding USEPA Equivalent methods for NPDES reporting. Many customers have requested letters from the EPA stating these methods' acceptance. Lachat would like to stress that the USEPA will not be issuing letters for methods that fall within the flexibility allowed at 40 CFR Part 136.6 of the EPA's Method Update Rule (MUR), March 2007, and that these methods **are acceptable** for NPDES compliance monitoring. A good example of this is Lachat method 10-107-04-1-C. Lachat Applications submitted the method for review to the USEPA, requesting a letter stating that the method was acceptable for use in both NPDWR and NPDES compliance monitoring. The modifications in this method allow samples to be analyzed without pH adjustment due to the high flow rate of the buffer reagent, which allows the method to compensate for high or low pH samples. This method adjustment falls within the flexibility allowed at 40 CFR Part 136.6 of the MUR. Therefore, this method is acceptable for use in NPDES compliance monitoring and no letter is required (or will be issued) by the EPA.

The EPA states that, ***"The absence of a letter does not preclude use of Equivalent Lachat methods for NPDES compliance monitoring purposes."*** The modifications that fall within the allowed flexibility of the MUR do not require review as a Clean Water Act ATP.

The USEPA sent Lachat and all Regional ATP Coordinators this statement regarding this issue:

"Due to increased inquiries on method flexibility we would like to stress:

Regions, States and permitting authorities should not expect a letter from the EPA's Office of Science and Technology (OST) stating that a modification that falls within the flexibility allowed under 40 CFR Part 136.6, which was added as part of the Methods Update Final Rule published in the Federal Register on March 12, 2007. Such modifications are acceptable for use in CWA monitoring. Letters for modified methods that fall within the scope of Part 136.6 will no longer be issued and the use of these methods are acceptable provided that they meet the performance requirements specified in the method.

Secondly, the flexibility allowed at Part 136.6 may be used to modify any method approved at Part 136 for compliance monitoring under the CWA including methods developed by VCSBs such as Standard Methods and ASTM International. If you choose to modify an approved method, in addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as Standard Methods, ASTM International or AOAC, International. This is further clarified in the attached memo from Richard Reding, Ph.D., Chief, EASB to Regional ATP Coordinators and Alternates titled: Citing Clean Water Act Limited-Use ATP Methods as Modifications dated April 14, 2008."

Please contact the EPA or Lachat Instruments for copies of the above-mentioned EPA correspondence.

EPA Contacts for MUR questions are:

CWA ATP Coordinator Lemuel Walker (walker.lemuel@epa.gov)

The CWA methods Team (OSTCWAMethods@epa.gov)

Lachat would love to hear about your lab's experiences with the MUR. Is the intent to allow for more flexibility helping your lab? Please send Lachat any comments, good or bad, on the MUR to Lachat Technical Support (support@lachatinstruments.com).

Appendix II

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

Date: April 14, 2008

To: Regional ATP Coordinators and Alternates

From: Richard Reding, Ph.D., Chief
Engineering and Analytical Support Branch
Engineering & Analysis Division, Office of Science & Technology

Topic: Citing Clean Water Act Limited-Use ATP Methods as Modifications

I am writing to our regional partners about citing a method for which a Region has issued a limited-use ATP approval letter that results in modifying another approved method. In addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as the Standard Methods Committee, AOAC, International, or ASTM, International.

For example, a lab with a CWA limited-use approval letter may conduct a luminescent measurement of dissolved oxygen (DO) with any approved method that requires a DO measurement, such as BOD or CBOD by SM5210B. However to do so, the lab will have a copy of a limited-use ATP approval letter. The lab SOP also will cite use of SM 5210B as "modified for luminescent measurement of DO in accordance with the limited-use ATP letter from the region" or similar wording.

Why do we recommend use of limited-use ATP approvals rather than wait for nation-wide approval? Because rulemaking can be a lengthy process. Thus in our national ATP letter, we recommend that regions consider approving use of the ATP under their limited-use ATP approval authority. Is it necessary for a limited-use ATP applicant to submit data, or do a side-by-side comparison in these cases? Our answer is generally no because methods that we review under the CWA ATP program already have multi-lab and comparability data.

Feel free to share this memo with your co-regulators, and the laboratory and method development community. Your contacts are the CWA ATP coordinator Lemuel Walker (walker.lemuel@epa.gov), or the CWA methods team (OSTCWAMethods@epa.gov).

cc: Lemuel Walker, CWA ATP coordinator
Steve Wendelken, SDWA ATP coordinator

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 30% Postconsumer)

Appendix III

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
REGION V
Surveillance and Analysis Division
536 South Clark St.
Chicago, Illinois 60605

JAN 9 1981

Roger L. DeRoos, Ph.D., Director
Division of Environmental Health
Minnesota Department of Health
717 Southeast Delaware Street
Minneapolis, Minnesota 55440

Dear Dr. DeRoos:

The Surveillance and Analysis Division, Region V, and the Environmental Monitoring and Support Laboratory (EMSL) - Cincinnati, of the U.S. Environmental Protection Agency, have carefully reviewed your Division's request of February 27, 1980, for approval of an alternate test procedure for ammonia analysis. The application specifies the proposed test procedure will be used by the Division of Environmental Health's Section of Analytical Services for the analysis of ammonia during monitoring for the National Pollutant Discharge Elimination System (NPDES).

The proposed methodology determines ammonia colorimetrically by first oxidizing ammonia to nitrite in alkaline hypochlorite solution using iodine as a catalyst. Reaction conditions are such that positive nitrite interference is removed prior to this reaction. Standard colorimetry is used to determine the nitrite resulting from the ammonia oxidation. Standard Auto Analyzer instrumentation is used for the above colorimetric analyses.

Ample data are provided to show the proposed methodology is equivalent to the distillation - Nesslerization reference method for a representative number of NPDES effluents in the State of Minnesota, and to show that it is more precise and sensitive than this same reference method. The proposed method is correctly justified as being more cost effective than the distillation - Nesslerization reference method.

On the basis of comparability data in your February 27th application, and on the basis of favorable recommendations of the two U.S. EPA reviewing offices, the Division of Environmental Health, Minnesota Health Department is authiorized to use the alternate test procedure, specifically described in your application of February 27, 1980, for the measurement of ammonia during NPDES monitoring in the State of Minnesota.

Appendix III (cont.)

- 2 -

Your laboratory staff is to be commended for implementing ammonia analyses of increased cost-effectiveness and precision of measurement.

Sincerely yours,

William H. Sanders III

William H. Sanders III, P.E.
Director

cc: A. Tupy, MNHD
J. Davenport, MPCA
R. Booth, EMSL - Cincinnati

S:\public\methods\sops.final-2000\General Chemistry SOPs (Final)\DP.COND.014.D05.doc

PROCEDURE FOR THE DETERMINATION OF:

CONDUCTIVITY IN WATER

Conductivity at 25°C - 14

1.0 SCOPE AND APPLICATION

1.1 Conductivity is a measure of water's ability to carry an electrical current. This property is related to the presence of ions, the total concentration of the ions, their mobility and valence and the temperature at which the measurement is made. Conductivity is the normalized measure of conductance that factors in the cell constant and temperature. The reciprocal of conductivity is resistivity. Solutions of most inorganic compounds (salts, acids, bases) have a high conductivity. Distilled or deionized water and water containing organics would have a low conductivity.

1.2 This Standard Operating Procedure (SOP) is applicable to the detection of conductivity in drinking, surface and saline waters, domestic and industrial wastes, and acid deposition samples. The quality of laboratory pure water (reagent water) can be monitored for conductivity, provided the sample is analyzed soon after collection. The conductivity of potable water generally ranges from 50 to 1500 µmhos/cm. The conductivity of distilled water is less than 2 µmhos/cm.

1.3 This SOP can be used for sample analysis under the Clean Water Act and is recommended for Safe Drinking Water Act (SDWA) monitoring.

1.4 The working range is 0.10 to 199,990 µmhos/cm. Working range of the reference method is 10 to 50,000 µmhos/cm.

1.5 This SOP is compliant with the requirements of Method 2510 B, Standard Methods, 20th Edition.

1.6 Storet Numbers:

Conductivity	00095

2.0 SUMMARY OF METHOD

2.1 The conductivity of a sample is measured by a conductivity meter and electrode. The meter sends an alternating voltage or current to the conductivity cell and measures the size of the resulting signal, which is linearly related to the conductivity. Samples are analyzed at 25°C, or temperature corrected by the meter and results reported at 25°C.

2.2 Results are reported in µmhos/cm. The standard unit of electrical conductance, the mho, is the reciprocal of the standard unit of electrical resistance, the ohm. The unit, Siemen, is the equivalent of the mho.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the Laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Reagent Blank (RB) immediately before any samples are analyzed and periodically throughout the run as needed.

4.2 Keep conductivity cells clean to prevent bad readings due to fouling of the electrode.

4.3 Rinse electrodes sufficiently to prevent carry-over from previous samples.

4.4 Conductivity increases with increasing temperature; to make accurate measurements it is important to compensate for deviations from the reference temperature of 25°C. This is done automatically by the instrument.

4.5 Exposure to air and the water container will increase conductivity readings; use fresh reagent water with each use.

5.0 SAFETY

5.1 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02	Occupational Safety and Health
420.01	Right-to-Know

In addition, the analyst should read the MDH Public Health Laboratory Division - Chemical Hygiene Plan. Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Safety Officer.

5.2 Safety glasses must be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.3 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A.

6.3 Conductivity meter, Orion 160.

6.4 Conductivity cell, immersion type.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent, freshly generated, with a resistivity > 16 megohm-cm at 25°C and a conductivity less than 2 µmhos/cm.

7.2 Only Analytical Reagent (AR)-grade or American Chemical Society (ACS)-grade chemicals should be used.

7.3 External QCS: Prepare according to manufacturer's instructions. As an alternative to purchasing a QCS, use solution in Section 7.4.

7.4 Standard potassium chloride solution, 0.01000 N KCl: To a 1-L volumetric flask containing about 800 mL of reagent water, dissolve 0.7455 g anhydrous KCl (dried at 105°C for two hours). Dilute to 1 L with reagent water. Store in glass-stoppered borosilicate glass bottle. Conductivity at 25°C is 1413 µmhos/cm.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected and stored in plastic 125-mL, 1-L or 2-L bottles and stored at 4°C prior to analysis.

8.2 No preservatives should be added to the samples. The conductivity analysis cannot be performed on an acidified sample.

8.3 Maximum holding time is 28 days. Samples with anticipated very low conductivity values should be analyzed as soon as possible.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability: The analyst must make an initial demonstration of capability to generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 External verification of instrument performance: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within ± 10% of the established QCS value; otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.2 Method detection limit (MDL) study: An MDL study is not possible with this analysis.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily calibration: A daily calibration is not required for this analysis.

9.2.2 External verification of instrument performance: Analyze a quality control sample (QCS) from the external source immediately after instrument warm-up to verify instrument performance. The results of the QCS must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.3 Demonstration of low background: At the beginning of the analytical run, analyze an initial calibration blank (ICB) or a laboratory reagent blank (LRB) to determine reagent or laboratory contamination. The background level of analyte must be below 1.0 µmhos/cm; otherwise, the source of the contamination is investigated and corrected before samples are analyzed.

9.2.4 Precision: Analyze a laboratory duplicate (LD) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. Calculations of the absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.3 External verification of laboratory performance: Performance evaluation (PE) samples are analyzed as required for Federal certification. If the results are not within the control limits, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance (QA) Officer.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Allow samples to come to room temperature (25°C).

10.2 Initially run a blank using fresh reagent water and then test the external reference sample. If reference result is within control limits, proceed with sample analysis.

11.0 PROCEDURE

11.1 Turn conductivity meter on to warm up (30 minutes).

11.2 Immerse the conductivity cell in fresh reagent water for a blank. Blanks should be under 1 µmhos/cm.

11.3 Place the conductivity cell in a Quality Control Sample (QCS) to verify instrument performance. Proceed with samples if the QCS is within control limits.

11.4 Rinse the conductivity cell with reagent water after reading the QCS.

11.5 Immerse the conductivity cell in the sample. Readings indicate the specific conductivity at 25°C. Record results on the bench sheet.

11.6 Note the units on the instrument display. The instrument auto-ranges between µmhos/cm (µS/cm) and mmhos/cm (mS/cm). Results are reported in µmhos/cm; therefore, results obtained in mmhos/cm need to be adjusted. See Section 12.5 for the calculation.

11.7 Rinse the conductivity cell with the reagent water and repeat for the remaining samples.

11.8 Analyze a laboratory duplicate (LD) for every 10 samples processed.

11.9 When analyses have been completed, rinse the electrode thoroughly with reagent water, dry it, and place it in a dry test tube rack for storage.

11.10 Write results on Conductivity bench sheet, with date of analysis, analysts' initials, and date of collection.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Readings are taken directly from the meter.

12.2 A method detection limit (MDL) cannot be calculated for this method.

12.3 The minimum reporting level is 0.2 µmhos/cm.

12.4 Results are reported in µmhos/cm to two significant figures.

12.5 The instrument auto-ranges between µmhos/cm (µS/cm) and mmhos/cm (mS/cm). To convert mmhos/cm to µmhos/cm, multiply the result by 1000.

12.6 Laboratory duplicates and the LRB are highlighted. The results for the QCSs are circled. The results are entered into the LIMS.

12.7 The average concentration of any laboratory duplicate analysis is reported.

12.8 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1. Information pertinent to our laboratory's performance can be found in our Quality Assurance Manual, Section 9.

13.2. Precision and accuracy data used for single laboratory testing will be summarized annually by the QA Officer.

14.0 POLLUTION PREVENTION

14.1. For information regarding the laboratory's pollution prevention policy and procedures see Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

14.2. The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3. For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1. The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reclamation, recycling, and purchasing.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Defined the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2. All waste from this SOP can be disposed of down the drain.

15.3. For additional information regarding the laboratory's waste management policy, see Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

16.0 BIBLIOGRAPHY

16.1. "Methods for Chemical Analysis of Water and Wastes." U.S. Environmental Protection Agency, Method 354.1, 1983.

16.2. Standard Methods for the Examination of Water and Wastewater, Method 2510 B, 20th Edition, 1998.

16.3. Instrument Manual, Orion 160.

17.0 DIAGRAMS, FLOWCHARTS, VALIDATION DATA

17.1 The initial Demonstration of Capability data is on file; precision and accuracy data are also on file in the Environmental Laboratory.

ORIGINAL

S:\public\methods\sops.final-2000\General Chemistry SOPs (Final)\DP.COND.014.D05.doc

Developed By: Lisa Dankert Date: 4/09/2001

Written By: Lisa Dankert Date: 4/09/2001

Revised By: Stephanie Peterson Date: 6/21/2005
Stephanie Peterson, Env Analyst 1

Approved By: Keith Peacock Date: 6/21/05
Keith Peacock, BactiChem Unit Supervisor

Reviewed By: William Scruton Date: 6/21/05
William Scruton, QA Officer

Approved By: Louise S. Liao Date: 6.21.05
Louise Liao, Env Lab Section Manager

Approved By: [signature] Date: 6-23-05
Norman Crouch, PHL Division Director

PROCEDURE FOR THE DETERMINATION OF: METALS BY INDUCTIVELY COUPLED PLASMA (ICP) ATOMIC EMISSION SPECTROSCOPY (AES) IN WATER, WASTE, AND SEDIMENT

1.0 SCOPE AND APPLICATION

1.1 This method has been developed for use by the Chemical Laboratory Section of the Minnesota Department of Health and provides analytical procedures for the determination of metal analytes in solution. This method is consolidated from existing methods for waters, soil/sediments, and solid wastes currently regulated by the Safe Drinking Water Act, Clean Water Act or the Resource Conservation Recovery Act.

1.2 This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5

Analyte		Chemical Abstract Services Registry Numbers (CASRN)
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	Unknown
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

1.3 Because of the differences between various makes and models of spectrometers, the analyst should follow the instrument manufacturer's instructions and, if possible, approximate the recommended conditions given in the method referenced.

1.4 When using this method for determination of boron and silica in aqueous samples, only plastic, Teflon or quartz labware should be used from the time of sample collection through completion of the sample analysis. For accurate determinations of boron in solid sample extracts at concentrations below 100 mg/kg, only quartz beakers should be used in the digestion procedure. Immediately transfer an aliquot of the digestate to a plastic centrifuge tube or volumetric flask and dilute to volume. Borosilicate glass must not be used for these determinations, in order to avoid sample contamination of these analytes from the glass.

1.5 This method is applicable to analysis of drinking water for the determination of primary and secondary contaminant metals.

1.6 This method is suitable for determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains < 0.1 mg/L silver.

1.7 The sample preparation procedures given in Sections 11.2 and 11.3 will solubilize and hold in solution only minimal concentrations of barium, as barium sulfate. In addition, the stability of solubilized barium is greatly affected when free sulfate is available in solution. The concentration of barium that will remain in solution decreases as the free sulfate concentration increases.

For example, when a 100 mL aliquot of drinking water containing 60 mg/L sulfate was fortified with 5 mg of $BaSO_4$ salt (equivalent to 59 mg/L Ba in the 2X analysis solution) only 33 mg/L Ba was initially solubilized using the procedure given Section 11.2.1. Upon standing one week, the barium concentration decreased to 12 mg/L. When 100 ml of deionized distilled water was fortified, the entire 5 mg of $BaSO_4$ was solubilized and remained in solution over the same time period.

To increase the accuracy of barium determinations in samples having varying and unknown concentrations of sulfate, samples should be analyzed as soon as possible after sample preparation is completed.

2.0 SUMMARY OF METHOD

2.1 This method describes the multi-element determination of metals and non-metals in solution by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES). The basis of the method is the measurement of atomic emission spectra by optical spectrometry.

An Inductively Coupled Plasma (ICP) source consists of a flowing stream of argon gas ionized by an applied radio frequency field, typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas (plasma) by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated by a nebulizer in the spray chamber and is carried into the plasma through the center tube located within the torch. The sample aerosol is swept directly into the plasma where desolvation and excitation occur, subjecting the constituent atoms to temperatures of about 10,000° K. This results in almost complete dissociation of molecules and a significant reduction in chemical interferences. The ICP provides an optically "thin" source that is not subject to self-absorption and is considered the optimal viewing zone for analytical determinations.

The efficient excitation provided by the ICP results in low detection limits for many elements. This, coupled with the extended dynamic range, permits effective multi-element determination of metals. The light emitted from the ICP is focused onto the entrance slit of either a monochromator or a polychromator that effects dispersion. A precisely aligned exit slit is used to isolate a portion of the emission spectrum for intensity measurement using a photomultiplier tube.

A monochromator uses a single exit slit and photomultiplier tube which uses a computer-controlled scanning mechanism to examine the emission wavelengths sequentially. A polychromator uses multiple fixed exit slits with a corresponding photodiode array which can simultaneously monitor all configured emission wavelengths using a computer-controlled readout system. The sequential approach provides greater wavelength selection while the simultaneous approach can provided greater sample throughput.

The analysis described in this method involves multi-element determinations by ICPAES using either sequential or simultaneous instruments. Both instrument types require a background correction technique to compensate for variable background contributions. Background must be measured adjacent to the analyte wavelength during analysis. Also, interferences (Section 4) related to ICPAES analysis must be recognized and corrected.

3.0 DEFINITIONS

3.1 Calibration Blank - A volume of ASTM type I water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.2 Calibration Standard (CAL) - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 Dissolved - The concentration of analyte that will pass through a 0.45 µm membrane filter assembly, prior to sample acidification.

3.4 Instrument Detection Limit (IDL) - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.5 Instrument Performance Check (IPC) Solution - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Internal Standard (IS) - A pure analyte(s) added to a sample, digest, or standard solution in know amounts and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

3.7 Laboratory Duplicates (LD1 and LD2) - Two aliquots of the sample taken in the laboratory and analyzed separately using identical procedures. Analyses of LD1 and LD2 indicate precision associated with the laboratory's analytical procedure but not with sample collection, preservation, or storage procedures.

3.8 Laboratory Fortified Blank (LFB) - An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether method performance is within acceptable control limits.

3.9 Laboratory Fortified Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for the concentration found.

3.10 Laboratory Reagent Blank (LRB) - An aliquot of reagent water that is treated exactly as a sample, including exposure to all glassware, equipment, reagents, and acids that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or apparatus.

3.11 Linear Calibration Range (LCR) - The concentration range over which the analytical curve remains linear.

3.12 Method Detection Level (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.13 Method of Standard Addition - The addition of a known amount of analyte to the sample in order to determine the relative response of the instrument to the analyte within the sample matrix. The relative response is then used to assess the samples analyte concentration.

3.14 Yttrium Solution - A solution that is used to determine the optimum height above the work coil for viewing the plasma.

3.15 Quality Control Sample (QCS) - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB matrix. The QCS is obtained from a source external to the laboratory and is used to check laboratory performance.

3.16 Stock Standard Solution - A concentrated solution containing one or more analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source. Stock standard solutions are used to prepare calibration solutions and other needed analyte solutions.

3.17 Spectral Interference Check (SIC) Solution - A solution of selected method analytes of higher level concentrations which is used to evaluate the procedural routine for correcting known inter-element spectral interferences with respect to a defined set of method criteria.

3.18 Total Recoverable - The concentration of an analyte determined in an unfiltered sample following treatment by refluxing with hot, dilute mineral acid.

3.19 Tuning Solution - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses.

4.0 INTERFERENCES

4.1 Several types of interference effects may contribute to inaccuracies in the determination of an analyte by Inductively Coupled Plasma Atomic Emission Spectroscopy. They can be summarized as follows:

4.1.1 Spectral interferences - Can be categorized as: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of raw data, requiring monitoring and measurement of the interfering element. The second effect may require selection of an alternative wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line.

Since inter-element spectral interferences can occur between method analytes when using the recommended wavelengths, the locations for background corrections must be determined and their correction factors calculated for each interfering element. The larger the correction factor the greater the interference. The interference effects must be evaluated for each individual instrumental system.

The correction factors should be determined by analyzing single element solutions of each interfering element. The concentration of each single element solution should also be within the linear dynamic range of that element. For most elements a 100 mg/L solution can be used to confirm most correction factors by analyzing lesser dilutions of the single element solution. Because Ca, Fe, Mg and Na can normally be present at concentrations in excess of 100 mg/L, the interferences attributed to these elements may need to be determined at concentrations near their linear limit.

The criterion for listing a spectral interference is an apparent analyte concentration from the interfering single element solution that is outside the 95% confidence interval estimated for the determined MDL of the analyte. The correction factor is calculated by dividing the blank subtracted analyte concentration by the determined concentration of the interfering element.

Positive values are interferences that occur on the wavelength peaks, while negative values indicate interference at the location used for background correction.

The correction factor is used to calculate the apparent concentration from interfering element and is then subtracted from the instrumental analyte concentration to determine the net, or sample analyte concentration (positive values are subtracted and negative values are added). Without these corrections, when interference effects are present, either false positive or false negative determinations will result. Also, the reliability of an applied correction depends on the variance surrounding the measurement of the interfering element.

As the concentration of the interfering element increases, the variance increases. This is reflected in the calculated apparent analyte concentration. Extreme caution should be exercised when reporting analyte concentrations where the apparent analyte concentration from an interfering element accounts for 90% of the measured analyte concentration.

Once a routine procedure for correcting inter-element spectral interferences has been established, it should be periodically tested to evaluate its operational effectiveness and continued reliability.

4.1.2 Physical interferences - Are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as a change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or high acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are present, they must be reduced by sample dilution and/or utilization of standard addition techniques.

Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. The use of a mass flow controller increases the regulation of the argon flow rate which can reduce the solids deposition while improving the instruments overall performance.

4.1.3 Chemical interferences - Are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of the operating conditions (i.e., incident power, torch height, etc.), by buffering the sample, matrix matching, or standard addition procedures. These types of interferences can be highly dependent on the matrix type and the specific analyte to be determined.

4.1.4 Memory interferences - Result when analytes in a previous sample contribute to the signals measured in the current sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer or from buildup of sample material in the plasma torch and spray chamber.

The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples. The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be determined and used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis.

This may be achieved by aspirating a standard containing elements corresponding to either their LDR or concentrations ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit should be noted.

Until the required rinse time is established, this method recommends a rinse period of 60 seconds between samples and standards. If a memory interference is suspected, the sample should be reanalyzed after an extended rinse period.

4.2 The occurrence of interferences described in Sections 4.1.1 through 4.1.3 is primarily attributed to the sample matrix. If an interference caused by a particular sample matrix is known, in many cases it can be circumvented. However, when the nature of the sample is unknown, tests as outlined in Sections 4.2.1 through 4.2.4 can be used to assure the analyst that either positive or negative interference effects are occurring with any of the elements. These interference effects may cause inaccuracies of the reported values if not detected.

4.2.1 Serial dilution - If the analyte concentration is sufficiently high (minimally a factor of 10X the MDL after dilution), the analysis of a dilution should agree within 10% of the original determination or within an established acceptable control limit. If not, a chemical or physical interference effect should be suspected.

4.2.2 Analyte addition - A post digestion analyte addition added at a minimum level of 20X the MDL (maximum 100X) to the original determination should be recovered to within 90% to 110% or within an established control limit. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Note: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternative wavelength, or comparison with an alternative method is recommended (Section 4.2.3).

4.2.3 Alternate method of analysis - When investigating a sample matrix, comparison with an alternative method of analysis may be required. The alternate method should be appropriate to the analyte concentration suspected or estimated (e.g., Atomic Absorption Spectrometry, ICP Mass Spectrometry, or other approved methodology).

4.2.4 Wavelength scanning of analyte line region - If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5.0 SAFETY

5.1 The analyst is required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	NAME
44.50-01	Occupational Safety and Health
66.00-01	Right-to-Know

In addition the analyst should read the MDH Public Health Laboratory Division - Chemical Hygiene Plan. Questions regarding the chemical hygiene plan should be referred to the Health and Safety Officer.

5.2 Safety glasses are required at all times while in the laboratory areas and all visitors to the laboratory area should be given temporary visitor safety glasses. Visitors' safety glasses are located near the front laboratory entrance.

5.3 The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.4 The analyst may contact the MDH Employee Hazard Hotline by calling the number posted on their phone.

5.5 The following guidelines are designed to aid the analyst in the safe operation of the atomic spectroscopy instrumentation and ancillary equipment:

5.5.1 Read and review all hazard and safety sections in the manufacturers reference/operating manuals. Particular attention should be addressed to areas that are highlighted, such as: Warning, Important, or Note.

Warning: Usually indicates an operation that could cause personal injury if precautions are not followed.

Important: Usually indicates an operation that could cause instrument damage if precautions are not followed.

Note: Usually indicates additional significant information is provided with the procedures.

5.5.2 Since high pressure gas cylinders are commonly used with atomic spectroscopy instrumentation the analyst should be familiar with the safe handling practices regarding the use of these cylinders.

5.5.3 Analytical plasma sources emit radio frequency radiation and intense UV radiation. Suitable precautions should be taken to protect the analyst from such hazards.

5.6 This information does not attempt to cover every safety procedure that should be practiced. Ultimately, maintenance of a safe laboratory environment is the responsibility of the analyst.

6.0 EQUIPMENT AND SUPPLIES

6.1 Analytical Instrumentation - The ICP instruments has a sequential spectrometer system that uses ionized argon gas as the plasma. The system and processing of background corrected signals is computer controlled. The instrument is capable of meeting and complying with the requirements and description of the technique given in Section 2.1 of the method. In particular, it is the responsibility of the analyst to investigate the spectral interference (Section 4.1.1) possible for each analytical wavelength used and to verify and periodically confirm that the instrument configuration and operating conditions used satisfies the analytical requirements.

6.1.1 Argon gas supply should be the liquid, high purity grade (99.99%).

6.1.2 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.3 Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more specific control of reproducible plasma conditions.

6.1.4 For routine analyses of solutions containing dissolved solids >1%, a high solids nebulizer and a torch injector tube having an inner diameter (i.d.) >1.0 mm are recommended.

6.1.5 For sustained analyses of solutions containing alkali concentrations >0.5%, an alumina torch injector tube is recommended to prevent devitrification of the normally used quartz injector tube.

Note: Regular periodic cleaning of the quartz torch assembly and injector tube by soaking in aqua regia (Section 7.1.9) reduces background signal noise, calibration drift and potential memory effects.

6.2 Labware - For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area, designated for trace element sample handling must be used.

Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, Teflon, etc.), including the sample container, should be cleaned prior to use.

Labware should be soaked overnight and thoroughly washed with laboratory grade detergent and water, rinsed with water, and soaked for four hours in a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with ASTM type I water, and oven drying if applicable.

Note: Chromic acid must not be used for cleaning glassware.

6.3.1 Glassware - volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.3.2 Pipettes - assorted calibrated pipettes and/or pipetters (with appropriate metal-free plastic tips).

6.3.3 Wash Bottle - one or two piece stem made of either low density polyethylene (LDPE) or Teflon (FEP) bottle with screw closure, 125 mL capacity or greater.

7.0 REAGENTS AND STANDARDS

7.1 Reagents - May contain elemental impurities which might affect analytical data. Only high purity reagents should be used whenever possible. All acids used for this method must be high purity or trace metal grade. Suitable acids are available from a number of manufacturers or vendors.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41/CASRN 7697-37-2).

7.1.2 Hydrochloric acid, concentrated (sp.gr. 1.19/CASRN 7647-01-0).

7.1.3 Aqua regia – Add 100 mL concentrated nitric acid to 300 mL concentrated hydrochloric acid and 100 mL ASTM type I water.

7.2 Water - For all sample preparation and dilutions, ASTM type I water as specified in ASTM Method D1193 is required.

7.3 Standard Stock Solutions - Are purchased from a reputable commercial source as single element stock standards or multi-element standards.

7.4 Mixed Calibration (CAL) Solutions

7.4.1 Although this method is applicable for the analysis of 31 analytes (Section 1.2), the laboratory currently only calibrates the instrument for the analysis of boron, calcium, Iron, potassium, magnesium, and sodium.

7.4.2 Prepare CAL solutions (Section 7.4.3) by combining appropriate volumes of the stock standard solutions in volumetric flasks. First, add the appropriate amount of conc. nitric acid, for a 2% nitric acid in final volume, followed by the appropriate stock standard aliquots and dilute with ASTM type I water. Transfer the freshly prepared mixed CAL solutions to an acid clean, not previously used Teflon or polyethylene bottles for storage. Fresh mixed CAL solutions should be prepared as needed with the realization that concentration can change upon aging.

7.4.3 The CAL solutions must be initially verified using a quality control sample and monitored weekly for stability. Although not specifically required, the listed CAL solution combinations should be followed when using the specified wavelengths and their respective background correction locations. If different combinations are used, the mixture should be verified for compatibility, stability and the absence of spectral interference between analytes. This same requirement would apply if a different wavelength was also utilized.

CAL Solution Ca & Mg Cal 9B (Volume = 200.0 mL)			
ANALYTE	STOCK SOLUTION mg/L	ALIQUOT VOLUME ml	ANALYTE CONCENTRATION mg/L
Ca	1000	10.0	50.0
Mg	1000	5.0	25.0

CAL Solution Sodium Cal 10 (Volume = 200.0 mL)			
ANALYTE	STOCK SOLUTION mg/L	ALIQUOT VOLUME ml	ANALYTE CONCENTRATION mg/L
Na	1000	10	50.0

CAL Solution Potassium Cal 2 (Volume = 250.0 mL)			
ANALYTE	STOCK SOLUTION mg/L	ALIQUOT VOLUME ml	ANALYTE CONCENTRATION mg/L
K	1000	5.0	20.0

CAL Solution Fe Cal 8 (Volume = 500.0 mL)			
ANALYTE	STOCK SOLUTION mg/L	ALIQUOT VOLUME ml	ANALYTE CONCENTRATION mg/L
Fe	1000	5.0	10.0

CAL High Std. 1 (Volume = 500.0 mL)			
ANALYTE	STOCK SOLUTION Mg/L	ALIQUOT VOLUME ml	ANALYTE CONCENTRATION mg/L
B	1000	5.0	10.0

7.5 Blanks - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve; a laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and a rinse blank is used to flush the instrument uptake system and nebulizer between standards and samples reducing memory interferences.

7.5.1 Calibration blank - Prepare by diluting a mixture of 10 mL of conc. nitric acid to 500 mL with ASTM type I water. Store in a Teflon bottle. If the sample matrix acid concentration is different from the above concentration every effort should be made to matrix match the calibration blank to that of the samples.

7.5.2 Laboratory reagent blank (LRB) - Contains all the reagents in the same volumes used in processing the samples. The LRB must be carried through the entire preparation procedure and analysis scheme. The final solution should contain the same acid concentrations as sample solutions for analysis.

7.5.3 Rinse blank - Prepare this acid wash solution in the same manner as the calibration blank except with the addition of a small amount of Triton X to help reduce surface tension and store in a convenient manner.

7.6 Instrument Performance Check (IPC) / QC21/7 Solution - This solution is prepared by adding the following listed aliquot volumes of the individual stock standards to the mixture of 2 mL nitric acid and diluting to 100 mL with ASTM type I water. Immediately transfer the freshly prepared LPC to an acid cleaned, preferably not previously used, sample bottle. See Table 7.8 at the end of Section 7.

7.7 Laboratory Fortified Blank (LFB) - To a 50 mL aliquot of ASTM type water add 1 mL of conc. nitric acid and 25 uL ICQ100-21 and 25 uL of ICQ100-7of the laboratory fortifying stock solutions. The LFB must be carried through the entire sample preparation procedure and analysis scheme. The final solution should be diluted to 50 mL as are the samples.

See Table 7.10 at the end of Section 7 for the expected concentration of each analyte based on the original 50 mL of water. This solution can also be prepared from a commercially purchased multi-element spiking solution. It is understood that a purchased multi-element spiking solution may not match the following concentrations exactly and that the laboratories actual spiking concentrations should be recorded.

7.12 Quality Control Sample - Quality control sample (IPC) should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L, except silver, potassium and silicon. See Table 7.8

TABLE 7.8
INSTRUMENT PERFORMANCE CHECK SOLUTION
(Final volume = 100mL)

ANALYTE	STOCK SOLUTION µg/mL	ALIQUOT VOLUME mL	CONCENTRATION µg/mL
Ag	50	1.0	0.5
Al	100	1.0	1.0
As	100	1.0	1.0
V	100	1.0	1.0
Ba	100	1.0	1.0
Be	100	1.0	1.0
Ca	100	1.0	1.0
Cd	100	1.0	1.0
Co	100	1.0	1.0
Cr	100	1.0	1.0
Cu	100	1.0	1.0
Fe	100	1.0	1.0
K	1000	1.0	10.0
Li	100	1.0	1.0
Mg	100	1.0	1.0
Mn	100	1.0	1.0
Mo	100	1.0	1.0
Na	100	1.0	1.0
Ni	100	1.0	1.0
Pb	100	1.0	1.0

TABLE 7.8 (Cont.)
INSTRUMENT PERFORMANCE CHECK SOLUTION
(Final volume = 100mL)

ANALYTE	STOCK SOLUTION µg/mL	ALIQUOT VOLUME mL	CONCENTRATION µg/mL
Sb	100	1.0	1.0
Se	100	1.0	1.0
Sr	100	1.0	1.0
Tl	100	1.0	1.0
Zn	100	1.0	1.0

TABLE 7.10
LABORATORY FORTIFIED BLANK (DS2)

ANALYTE	STOCK SOLUTION µg/mL	ALIQUOT VOLUME uL	CONCENTRATION µg/mL
Ag	100	500	1.0
Al	100	500	1.0
As	100	500	1.0
B	100	500	1.0
Ba	100	500	1.0
Be	100	500	1.0
Cd	100	500	1.0
Co	100	500	1.0
Cr	100	500	1.0
Cu	100	500	1.0
Fe	100	500	1.0
Li	100	500	1.0
Mn	100	500	1.0
Mo	100	500	1.0
Ni	100	500	1.0

TABLE 7.10 (Cont.)
LABORATORY FORTIFIED BLANK

ANALYTE	STOCK SOLUTION µg/mL	ALIQUOT VOLUME uL	CONCENTRATION µg/mL
Pb	100	500	1.0
Sb	100	500	1.0
Se	100	500	1.0
Sn	100	500	1.0
Sr	100	500	1.0
Tl	100	500	1.0
V	100	500	1.0
Zn	100	500	1.0
Ca	100	500	1.0
Mg	100	500	1.0
K	100	500	1.0
Na	100	500	1.0

ANALYTE	STOCK SOLUTION µg/mL	ALIQUOT VOLUME uL	CONCENTRATION µg/mL
Ca	10000	450	9
Mg	10000	450	9
K	10000	450	9
Na	10000	450	9

Note: Two solutions required to achieve the 10 µg/mL concentration of Ca, Mg, K, Na. 450 ul of the 10000 µg/mL solutions above is spiked along with the 500 ul of the 100 µg/mL multi standard solution to achieve the 10 µg/mL.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Prior to collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation, etc., should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 For determination of dissolved elements, the sample must be filtered through a 0.45 µm membrane filter. Glass or plastic filtering apparatus is recommended to avoid possible contamination. Plastic apparatus should be used when determination of boron or silica is critical (Section 1.6). Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Immediately following filtration, acidify the filtrate to a pH < 2 with concentrated nitric acid (normally, 1 mL of acid per 500 mL of sample is sufficient for most filtered water samples).

8.3 For the determination of total recoverable elements in aqueous samples, acidify with concentrated nitric acid at the time of collection to a pH < 2 (normally, 1 mL of acid per 500 mL of sample is sufficient for most ambient and drinking water samples). The sample should not be filtered prior to analysis.

8.4 Solid samples usually require no preservation prior to analysis other than storage at 4°C.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and analysis of laboratory reagent blanks and fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.

9.2 Initial Demonstration of Performance

9.2.1 The initial demonstration of performance is used to characterize instrument performance (method detection limits and linear calibration ranges) and laboratory performance (analysis of quality control samples) for analyses conducted by this method.

9.2.2 Linear calibration ranges - The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. Linear calibration ranges should be determined whenever there is a significant change in instrument response and every six months for those analytes that periodically approach their linear limit. The current practice of the laboratory is to dilute and re-analyze all samples where an analyte concentration is above the highest acceptable calibration standard from the linear calibration range study.

9.2.3 External verification of calibration: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within 10% of the established QCS value; if it is not, the source of the problem must be identified and corrected before proceeding on with the initial determination of method detection limits.

9.2.4 MDLs should be established for all analytes, using reagent water (blank) fortified at a concentration of two to three times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where: t =Student's value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S =Standard deviation of the replicate analyses.

MDLs should be determined every six months or whenever there is a significant change in the background or instrument response.

9.2.5 Quality Control Sample (QCS) - When beginning the use of this method and on a quarterly basis, verify acceptable laboratory performance with the preparation and analyses of a quality control sample. The QCS is carried through the entire analytical operation of the method. If the determined concentrations are not within ±10% of the stated values of 1 mg/L, laboratory performance is unacceptable. The source of the problem should be identified and corrected before continuing analyses.

9.2.6 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.3 Assessing Laboratory Performance - Reagent and Fortified Blanks

9.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB with each set of samples. LRB data is used to assess contamination from the laboratory environment. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

9.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery. If the recovery of any analyte falls outside the control limits, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 Laboratory performance is assessed against target recovery limits of 85-115% for LFB's. Every 6 months the QC data for each method is compiled and compared to the target limits.

9.4 Assessing Analyte Recovery - Laboratory Fortified Sample Matrix

9.4.1 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. Ideally for water samples, the analyte concentration should be the same as that used in the LFB. This is also recommended for solid samples, however, the concentration added should be expressed as µg/g and calculated by multiplying the values given in Section 7.11 by the factor 100. Over time, samples from all routine sample sources should be fortified.

9.4.2 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 9.3.3 for the analyses of LFB's. Recovery calculations are not required if the concentration added is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where:
R =percent recovery.
C_s =fortified sample concentration.
C =sample background concentration.
s =concentration equivalent of analyte added to the sample.

9.4.3 If recovery of any analyte falls outside the designated range and laboratory performance for that analyte is shown to be in control, the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to matrix effects and analysis by method of standard addition should be considered.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Recommended wavelengths and background correction locations are listed in the method referenced. Other wavelengths and background correction locations may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. In Section 17 specific instrument operating conditions are recommended. However, because of the difference among various makes and models of spectrometers, the analyst should follow the instrument manufacturer's instructions, and if possible, approximate the recommended operating conditions.

10.2 Allow the instrument to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to plasma optimization, plasma tuning and/or calibration.

10.3 Plasma Optimization - Prior to the use of this method optimize the plasma operating conditions using the following procedure. The purpose of plasma optimization is to provide a maximum signal to background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

10.3.1 Select an appropriate incident radio frequency (RF) power with minimum reflected power and aspirate the 1000 µg/mL solution of yttrium. Following the instrument manufacturer's instructions, adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5 to 20 mm above the top of the work coil. Record the nebulizer gas flow rate or pressure setting for future reference.

10.3.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min by aspirating a known volume acid blank for a period of at least 3 minutes. Divide the spent volume by three and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

10.3.3 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions and aspirate the plasma tuning solution, containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14 to 18 mm above the top of the work coil (this region of the plasma is commonly referred to as the analytical zone). Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting.

Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the best compromise of intensity ratios of all four analytes.

10.3.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable Instrument Detection Level (IDL) and Method Detection Level (MDL).

10.3.5 If either the instrument operating conditions (such as incident power and/or nebulizer gas flow rate) are changed, or a new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be re-optimized.

10.3.6 Before daily calibration and after the instrument warm up period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be either reset to the recorded optimized flow rate or the optional plasma tuning procedure given in Section 9.4 should be followed to reconfigure the plasma. In order to provide and maintain valid inter-element spectral correction factors the nebulizer gas flow rate must be well controlled.

10.4 Plasma Tuning (Optional) - This procedure can be used on a daily basis to collect the data necessary for fine tuning the plasma to a set (Cu/Pb concentration ratio that reflects the optimized conditions. The analytical zone of the plasma can be altered by varying the aerosol carrier gas flow entering the plasma. This procedure requires the use of a mass flow controller for adjusting the nebulizer gas flow rate to reset the Cu/Pb concentration ratio. (This procedure can be used even when the front surface entrance optics degrade in a non-uniform manner over the visible and ultraviolet wavelength regions.)

10.4.1 Set the instrument to the optimized operating conditions. After instrument warm up, horizontal alignment of the plasma and/or optical profiling of the spectrometer, aspirate the plasma tuning solution and collect 10 replicate measurements of the Cu (324.75 nm) and Pb (220.35 nm) intensity signals at every 25 mL/min interval over the flow rate range of 500 to 800 mL/min. Repeat the operation using the calibration blank solution. Subtract the respective mean blank value and calculate the net mean intensity value for both metals at each flow rate. Plot the net mean intensity values versus flow rate. From the plot determine the maximum signal intensity flow rate for each metal.

10.4.2 To determine the Cu/Pb concentration ratio, set the instrument to the optimized operating conditions. After warm up and optical profiling, calibrate the instrument for both Cu (324.75 nm) and Pb (220.35 nm) at their respective maximum intensity flow rates with the calibration blank set at the optimum flow (e.g., 620 mL/min).

10.4.3 Reset the nebulizer gas flow to the rate (e.g., 620 mL/min) and collect data from 10 replicate analyses of the tuning solution. Ratio the determined copper concentration to the determined lead concentration on each analysis and compute the standard deviation and mean value of the 10 ratios. (Note: Disregard the fact that the determined concentrations do not equal the prepared concentrations of the tuning solution.) The mean value is used for resetting the ratio.

10.4.4 For tuning the plasma on a regular basis calibrate the instrument as described in Section 10.5. Reset the nebulizer gas flow rate to the optimum flow (e.g. 620 mL/min) and analyze the tuning solution. Calculate the Cu/Pb concentration ratio from the analysis. If the calculated ratio is not within two standard deviations of the mean value, adjust the nebulizer gas flow and reanalyze the tuning solution until the ratio is within range. Lowering the gas flow rate will increase the lead concentration, decrease the copper concentration, and, therefore, lower the ratio. The opposite is true when the gas flow is increased. Day-to-day variations in the nebulizer gas flow should be $< \pm$ 10 mL/min. Larger changes should alert the analyst to possible instrumental problems.

10.4.5 Once an acceptable ratio is achieved, the instrument is ready for analytical calibration.

10.4.6 If either the selected instrument operating conditions are changed or instrument components are replaced that require the plasma to be re-optimized, the Cu/Pb concentration ratio must be reestablished.

10.5 Calibration - Calibrate the instrument according to the instrument manufacturer's instructions using the prepared calibration blank and CAL solutions (Section 7.4). The following operational steps should be used for both CAL solutions and samples.

10.5.1 Using a peristaltic pump, introduce the standard or sample into the nebulizer at a uniform rate (e.g. 1.2 mL/minute).

10.5.2 To allow equilibrium to be reached in the plasma, aspirate the standard or sample solution for 30 seconds after reaching the plasma before beginning integration of the background corrected signal.

10.5.3 When possible use the average value of four 5 second background corrected integration periods as the atomic emission signal to be correlated to analyte concentration.

10.5.4 Between each standard or sample, flush the nebulizer and solution uptake system with the rinse blank acid solution for 60 seconds or for the required period of time to ensure that analyte memory effects are not occurring.

10.6 Analyze the LPC solution and calibration blank immediately following calibration, after every tenth sample and at the end of the sample run. The analyzed value of each analyte in the LPC solution should be within 90% to 110% of its expected value. If an analyte value is outside the interval, reanalyze the LPC. If the analyte is again outside the ± 10% limit, the instrument should be recalibrated and all samples following the last acceptable LPC solution should be reanalyzed.

10.7 Periodically verify the validity of the inter-element spectral interference correction process. The frequency of this testing is the responsibility of the analyst, however, confirmation prior to analysis of solid sample extracts is particularly useful.

10.8 If methods of standard addition are required, the following procedure is recommended.

10.8.1 The standard addition technique involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus producing a different slope from that of the calibration standards. It will not correct for additive interference that causes a baseline shift. The simplest version of this technique is the single addition method. The procedure is as follows: two identical aliquots (Volume V_x) of the sample solution, are taken; to the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s, to the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_S c_S}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x, and thus c_s is much greater than c_x, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For results from this technique to be valid, the following limitations must be taken into consideration:

- The analytical curve must be linear.

- The chemical form of the analyte added must respond the same as the analyte in the sample.
- The interference effect must be constant over the working range of concern.
- The signal must be corrected for any additive interference.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

For the determination of dissolved analytes in ground and surface waters, take a 50ml aliquot from a well mixed, acid preserved sample and add 1 ml of nitric acid and transfer it to an autosampler tube. The sample is now ready for analysis.

If a precipitate is formed during acidification, transport or storage, the sample aliquot must be treated using correct digestion procedure.

11.2 Sample Analysis

11.2.1 Analyze the samples by the procedural routine described in Sections 10.5, 10.6 and 10.7. If method of standard additions are required, follow the instructions given in Section 10.8. Samples having concentrations higher than the calibration range should be diluted into range and reanalyzed. The sample may first be analyzed for trace analytes providing the elements in high concentration do not cause a severe matrix effect and any inter-element spectral interference or shift in background intensity can be properly corrected.

11.2.2 For drinking water compliance monitoring, if the concentration of a primary contaminant is determined to be 90% of its MCL or above and the combined Mg and Ca concentration equals 500 mg/L, the sample should be analyzed by the standard addition technique (Section 10.8).

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data should be reported in units of µg/L or mg/L for aqueous samples and ug/g dry weight for solid samples. Do not report element concentrations below the determined MDL.

12.2 For aqueous samples prepared by total recoverable procedure, multiply solution concentrations by appropriate dilution factor and report the data in µg/L to two significant figures.

12.3 If dilutions were performed or if a drinking water sample was preconcentrated for analysis, the appropriate factor must be applied to sample values.

12.4 The QC data obtained during sample analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 METHOD PERFORMANCE

13.1 Precision and accuracy data used for single laboratory testing will be summarized every 6 months by the QA Officer.

14.0 POLLUTION PREVENTION

14.1 Public Health Laboratory Division Pollution Prevention Policy, Public Health Laboratory Hazardous Waste Manual, DRAFT, October 1994.

15.0 WASTE MANAGEMENT

15.1 Public Health Laboratory Division Waste Management Policy, Public Health Laboratory Hazardous Waste Manual, DRAFT, October 1994.

15.1.1 The Public Health Laboratory in carrying out its mission will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reclamation, recycling , and purchasing.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

16.0 REFERENCES

16.1 EPA Method 200.7, EPA Methods for the Determination of Metals in Environmental Samples, EPA/600/4-91/010, June, 1991.

16.2 "Standard Methods for the Examination of Water and Wastewater," 20th Edition, Method 3120-B, 1998.

16.3 Chemical Hygiene Plan, Public Health Laboratory Division Chemical Hygiene Plan, May, 1994.

16.4 Department of Health Policies and Procedures, Minnesota Department of Health Policy and Procedure Manual, October, 1992.

16.5 Public Health Laboratory Division Pollution Prevention Policy, Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

16.6 Public Health Laboratory Division Waste Management Policy, Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE A
EPA Method References and MDH Analyte Codes

Analyte	EPA Method	MDH Analysis Codes
Aluminum	200.7	630, 631, 632, 103, 101, 102
Antimony	200.7	635, 607, 608, 609, 216, 217
Arsenic	200.7	110, 638, 639, 111, 108, 109
Barium	200.7	117, 113, 114, 119, 115, 116
Beryllium	200.7	640, 641, 642, 222, 220, 221
Boron	200.7	617, 614, 616, 618
Cadmium	200.7	124, 125, 128, 126, 122, 123
Calcium	200.7	208, 251, 252, 210
Chromium	200.7	131, 132, 135, 134, 129, 130
Cobalt	200.7	138, 140, 139, 136, 137
Copper	200.7	147, 145, 146, 149, 143, 144
Iron	200.7	156, 152, 154, 155, 150, 151
Lead	200.7	160, 159, 647, 161, 157, 158
Lithium	200.7	627, 628, 629, 226, 227
Magnesium	200.7	209, 253, 254, 211
Manganese	200.7	170, 166, 168, 169, 164, 165
Molybdenum	200.7	230, 633, 634, 231, 228, 229
Nickel	200.7	175, 173, 174, 176, 171, 172
Phosphorus	200.7	---
Potassium	200.7	644, 255, 256, 212
Selenium	200.7	180, 184, 178, 179
Silica	200.7	---
Silver	200.7	187, 189, 185, 186
Sodium	200.7	645, 257, 258, 213
Titanium	EMMC	242, 243, 246, 244, 245
Vanadium	200.7	247, 651, 652, 650, 248, 249
Zinc	200.7	648, 194, 195, 196, 192, 193

TABLE B
Inductively-Coupled Plasma Instrument Operating Conditions

Incident RF Power:	950 – 1150 Watts
Reflected RF Power:	< 5 Watts
Viewing Height Above Work Coil:	16 mm
Injector Tube Orifice ID:	1 mm
Argon Supply:	Liquid Argon
Argon Pressure:	32-45 psi
Coolant Argon Flow Rate:	19 L/minute
Aerosol Carrier Argon Flow Rate:	620 mL/minute
Auxiliary (Plasma) Argon Flow Rate:	300 mL/minute
Sample Uptake Rate Controlled to:	1.2 mL/minute

Note: Refer to Scan Parameters in the method file for the current operating conditions.

Procedure Developed By: Robert C. Clark Date: 04/16/04

Procedure Written By: Robert C. Clark Date: 04/16/04

Procedure Reviewed By: Jeffry Brenner (Unit Leader) Date: 04/16/04

Date: 04/16/04
(QA Officer)

Procedure Approved By: Jean Kahlainen (Program Manager) Date: 4/19/04

PROCEDURE FOR THE DETERMINATION OF:

TRACE METALS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY

INCLUDES ALL ICP AND FURNACE ANALYSIS CODES
AND THE FOLLOWING

MDH CODES:		TOTAL	DISSOLVED
SDWA List 1		751	—
Antimony	Nickel		
Arsenic	Sodium		
Beryllium	Thallium		
SDWA LIST 2		752	—
Barium			
Cadmium			
Chromium			
Selenium			
SDWA List 3		753	—
Antimony	Chromium		
Arsenic	Nickel		
Barium	Selenium		
Beryllium	Sodium		
Cadmium	Thallium		
SDWA Cu/Pb		755	—
Copper			

MDH CODES:		TOTAL	DISSOLVED
Bottle Blanks		760	—
Aluminum	Lithium		
Antimony	Manganese		
Arsenic	Molybdenum		
Barium	Nickel		
Beryllium	Selenium		
Cadmium	Silver		
Chromium	Thallium		
Cobalt	Titanium		
Copper	Vanadium		
Lead	Zinc		
GW Special Scan, water		761	762
Aluminum	Lithium		
Arsenic	Magnesium		
Barium	Manganese		
Beryllium	Molybdenum		
Boron	Nickel		
Cadmium	Potassium		
Calcium	Silver		
Chromium	Sodium		
Cobalt	Strontium		
Copper	Titanium		
Iron	Vanadium		
Lead	Zinc		
Water Scan 9		763	764
Arsenic	Copper		
Barium	Lead		
Cadmium	Manganese		
Chromium	Nickel		
	Zinc		

MDH CODES:		TOTAL	DISSOLVED
Water Scan 18		765	766
Aluminum	Lead		
Antimony	Manganese		
Arsenic	Molybdenum		
Barium	Nickel		
Beryllium	Selenium		
Cadmium	Silver		
Chromium	Thallium		
Cobalt	Vanadium		
Copper	Zinc		
Special Scan, water		771	—
Cadmium	Molybdenum		
Chromium	Nickel		
Copper	Vanadium		
Lead			
RCRA 7, Total		775	—
Arsenic	Lead		
Barium	Selenium		
Cadmium	Silver		
Chromium			

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water according to U. S. EPA Method 200.8 using the HP 4500 ICP-MS. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and solid waste samples.

1.2 Dissolved elements in samples with turbidities greater than 1 NTU are determined after suitable filtration and acid preservation. Acid digestion procedures are required prior to determination of total recoverable elements. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v).

1.3 This method is applicable to the following elements:

Element		Chemical Abstract Services Registry Numbers (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-39-3
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Mercury	(Hg)*	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Thorium	(Th)*	7440-29-1
Uranium	(U)*	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

* Listed in method but not currently used as a method of analysis for that element.

1.4 This method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. Higher silver concentrations require dilution prior to analysis.

1.5 This method is approved for SDWA analysis.

1.6 Applicable USEPA MCL values are:

Antimony	6.0	µg/L
Arsenic	50.0	µg/L
Barium	2000.	µg/L
Beryllium	4.0	µg/L
Cadmium	5.0	µg/L
Chromium	100	µg/L
Selenium	50	µg/L
Thallium	2	µg/L

1.7 Reference methods:

EPA Method 200.8
Standard Methods (20th Ed). 3125B
EPA Method 1638

2.0 SUMMARY OF METHOD

2.1 This method describes the multi-element determination of trace elements by ICP-MS. Aqueous sample material (waters, digestates and leachates) are introduced by pneumatic nebulization via a spray chamber into a radio frequency argon plasma. Desolvation, atomization and ionization create predominantly singly-charged cations which are identified and quantitated by the use of a quadrupole mass spectrometer. Potential interferences from isobaric elements and polyatomic ions are corrected for by the use of elemental interference equations based on natural isotope abundances. Instrument drift and matrix induced signal suppressions and enhancements are compensated for by the use of internal standardization.

3.0 DEFINITIONS

3.1 Definitions applicable to this method:

Analysis Batch - A sequence of samples, which are analyzed within an analytical run and include no more than 10 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 10.

Calibration Blank - A volume of reagent water preserved the same as the calibration standards. The calibration blank is a zero standard used to calibrate the instrument.

Calibration Standard (CAL) - A solution or solutions prepared from the dilution of stock standard solutions. They are used to calibrate the response of the instrument with respect to analyte concentration.

Continuing Calibration Blank (CCB) - A laboratory reagent blank that is run with each batch of samples and at the end of the analysis run. The CCB may indicate contamination, carryover, baseline drift or other changes occurring over the course of an analytical run.

Continuing Calibration Verification (CCV) - A CAL solution or calibration standard which is analyzed after a prescribed number of samples (see QC section 9), which verifies the previously established calibration curve and confirms accurate analyte quantitation for all samples analyzed since the last calibration verification. The concentration of the CCV should be at the mid-point of the calibration curve. CCV is the same as Continuing Calibration Check Standards (CCCS).

Dissolved Analyte - The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter prior to sample preservation.

Field Blank (FB) - An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, storage, preservation, and all analytical procedures, which may include filtration. The purpose of the field blank is to determine if the field or sample transportation procedures and environments have contaminated the sample.

Field Duplicates (FD1 and FD2) - Two separate samples collected in separate sample bottles at the same time and place, under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

Filter Blank - Laboratory (FBL) - This is applicable when the client requests that the laboratory filter samples for a dissolved analyte. For each batch of lab-filtered samples, one FBL is taken through the procedure. Reagent water is passed through a 0.45µm filter and the filtrate retained and analyzed for the analyte of interest.

Initial Calibration Verification (ICV) - A CAL solution or calibration standard which is analyzed initially, prior to any sample analyses, which verifies the previously established calibration curve. ICV is the same as Initial Calibration Check standards (ICCS).

Instrument Performance Check Solution (IPC) - A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria. This is often a mid-level calibration standard analyzed at set intervals during a sample run to monitor the instrument performance.

Intermediate Standard - A solution made up from the stock standard solution and diluted as necessary to prepare working calibration solutions.

Laboratory Control Sample - A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system. For example, laboratory fortified blank or QC check sample.

Laboratory Duplicates (LD1 and LD2) - Two aliquots taken in the laboratory from a single sample bottle and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

Laboratory Fortified Blank (LFB) - An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The source of the added analytes can be from the source (manufacturer) of the calibration standards or from an external source. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is in control and whether the laboratory is capable of making accurate and precise measurements.

Laboratory Fortified Sample Matrix (LFM) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The source of the added analytes can be from the source (manufacturer) of the calibration standards or from an external source. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for the background concentrations found.

Linear Calibration Range (LCR) or Linear Dynamic Range (LDR) - The concentration range over which the instrument response to an analyte is linear.

Material Safety Data Sheet (MSDS) - Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

Matrix Spike (MS) - Aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample. Its purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS corrected for background concentrations. MS is the same as LFM.

Matrix Spike (MS) and Matrix Spike Duplicate (MSD) - Two aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations. MS is the same as LFM.

Maximum Contaminant Level (MCL) - The maximum permissible level of a contaminant in water which is delivered to the free flowing outlet of the ultimate user of a public water system.

Method Detection Limit (MDL) - The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined according to procedures in 40 CFR, Part 136, Appendix B.

Performance Evaluation (PE) sample or Performance Testing (PT) sample - A reference sample provided to a laboratory for the purpose of demonstrating that the laboratory can successfully analyze the sample within limits of performance specified by the USEPA. The true value of the concentration of the reference material is unknown to the laboratory at the time of the analysis.

Quality Assurance - A definitive plan for laboratory operation that specifies the measures used to produce data of known precision and accuracy.

Quality Control - A set of measures within a sample analysis methodology to assure that the process is in control.

Quality Control Sample (QCS) - A solution of method analytes of known concentrations which is used to check laboratory performance. The QCS is obtained from a source (manufacturer) external to the laboratory and different from the source (manufacturer) of calibration standards. The source of the QCS, or the QCS itself, can be used to fortify an aliquot of LRB or sample matrix.

Reagent Blank (RB) - An aliquot of reagent water or other blank matrix that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, reagents, acids, internal standards and surrogates that are used with samples. The RB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus that would affect sample preparation or analysis. Same as Laboratory Reagent Blank (LRB), Laboratory Blank, Preparation Blank and Method Blank.

Reagent Water - ASTM Type I or equivalent, free of the analyte of interest.

Report Level - The lowest concentration that can be reliably measured within specified limits of precision and accuracy during routine laboratory operating conditions at the MDH laboratory.

Stock Standard Solution - A concentrated solution containing one or more method analytes that is prepared in the laboratory or purchased from a commercial source. The intermediate standards or calibration standards are made up from dilutions of a stock standard solution.

Total Recoverable Analyte - The concentration of analyte determined by analysis of the solution extract of an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s).

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Reagent Blank (RB) immediately before any samples are analyzed and periodically throughout the run as needed.

4.2 For the determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust etc. A clean laboratory work area, designed for trace element sample handling must be used. Standards, samples and blanks should be exposed to the laboratory environment as little as possible. The use of preparation blanks and spikes should be used to verify the absence of sources of contamination and loss. If necessary, polypropylene sample tubes should be rinsed and stored in dilute acid prior to use.

NOTE: Chromic acid must not be used for cleaning glassware for trace metals analysis.

4.3 There are three fundamentally different sources of interference in ICP-MS:

4.3.1 Spectroscopic Interferences are interferences caused by the presence of compounds or elements entering the mass spectrometer, which have the same nominal mass to charge (m/z ratio as the analyte elements. They can be isobaric, polyatomic, refractory oxide, and doubly charged ions. Isobaric interferences are caused by isotopes of other elements or polyatomic species, which have the same nominal mass/charge ratio as the analyte element. These can be managed by the selection of an alternate isotope for analysis or by the use of elemental interference equations. These equations use the naturally occurring isotope ratios of most elements to estimate and allow for the subtraction of isobaric interferences. An example of an elemental isobaric interference is ^{40}Ar on ^{40}Ca, in this case the use of 43Ca or ^{44}Ca is recommended. A polyatomic isobaric interference is $^{40}Ar^{35}Cl$ on ^{75}As. In this case the use of an equation based on the isotopic abundances of $^{35}Cl/^{37}Cl$ would be used. A detailed description on the theory and use of elemental equations is contained in chapter 4 of the Agilent 4500 Application Handbook along with recommended equations and their derivations.

4.3.1.1 Most commonly used corrections for isobaric interferences are already included as the default equations in the default EPA 200.8 method included with this SOP. A list of the correction equations used is included in Table A1.

4.3.1.2 Care must be taken that any isotope used for correction purposes is itself not subject to uncorrected isobaric interferences.

4.3.2 Physical Interferences are associated with the physical processes, which govern the transport of sample into the plasma, sample conversion process within the plasma and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the samples and calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g. viscosity effects), at the point of aerosol formation and transport to the plasma (e.g. surface tension effects), during the atomization and ionization process within the plasma itself, or during the transfer of ions through the interface and mass spectrometer (space charge effects). To minimize some of these effects, acid composition and concentration should be matched for all standards, blanks and samples. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards should ideally display similar analytical behavior to the elements being determined.

To this end, internal standards should be matched as closely as possible to the analyte elements in mass, ionization potential, solubility, boiling point and reactivity to the various components in the sample introduction system. The recommended internal standards are listed in Table A3.

4.3.3 Memory Interferences result when elements in a previous sample contribute to signals measured in a subsequent sample. Memory effects can result from the deposition of sample on various components of the sample introduction system, including sample and peristaltic pump tubing, spray chamber, torch, and interface cones. The site(s) where deposition may occur is dependent on the sample and may need to be minimized through the use of a rinse blank between samples. Routine maintenance (cleaning and/or replacement) of sample introduction components is necessary for long-term minimization of memory effects. The possibility of memory interferences within an analytical run should be recognized and suitable rinse times should be used to reduce them. Memory effects are evaluated by using a minimum of three replicate integrations for data acquisition.

High relative standard deviation (%RSD) of the three replicates caused by a consecutive drop in signal intensity is indicative of carryover from the previous sample. If a memory interference is suspected, the sample should be reanalyzed after analysis of a blank indicates that the carryover has been eliminated.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this method has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02	Occupational Safety and Health
420.01	Right-to-Know

In addition, the analyst should read the MDH Public Health Laboratory Division - Chemical Hygiene Plan. Questions regarding the Chemical Hygiene Plan should be referred to the Health and Safety Officer.

5.3 Safety glasses must be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.4 The analyst may contact the MDH Employee Health and Safety Information Hotline regarding chemicals used in this procedure by calling the number posted in the laboratory.

5.5 The following guidelines are designed to aid the analyst in the safe operation of the atomic spectroscopy instrumentation and ancillary equipment:

5.5.1 Read and review all hazard and safety sections in the manufacturers reference/operating manuals. Particular attention should be addressed to areas that are highlighted, such as: Warning, Important, or Note.

Warning: Usually indicates an operation that could cause personal injury if precautions are not followed.

Important: Usually indicates an operation that could cause instrument damage if precautions are not followed.

Note: Usually indicates additional significant information is provided with the procedures.

5.5.2 Since high pressure gas cylinders are commonly used with atomic spectroscopy instrumentation the analyst should be familiar with the safe handling practices regarding the use of these cylinders.

5.5.3 Analytical plasma sources emit radio frequency radiation and intense UV radiation. Suitable precautions should be taken to protect the analyst from such hazards.

5.6 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.6.1 Concentrated nitric acid.

5.7 Use caution when handling strong acids and acid solutions. Always wear gloves, lab coat and eye protection.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipets are Class A.

6.3 Calibrated mechanical pipettes in the following ranges

10-100 µ
100-1000 µL
1000-5000 µL

6.4 Trace metal grade pipette tips.

6.5 Talc free gloves.

6.6 14 mL polypropylene test tubes for samples (Fisher Scientific #14-956-7E) and 50 mL polypropylene centrifuge tubes for standards (Fisher Scientific part # 14-375-150)

6.7 Argon gas supply (high purity grade gas or liquid, 99.99%)

6.8 HP 4500 ICP-MS system

6.8.1 Includes Agilent 4500 ICP-MS Instrument, ChemStation, Hewlett Packard LaserJet printer, Cetac ASX-500 Autosampler, and Neslab CFT 100 Refrigerated Recirculator.

6.8.2 Instrument Consumables (see manufacturer's literature).

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I (ASTM D 1193) or equivalent with a resistivity > 18 megohm-cm at 25° C. and free of the analytes of interest.

7.2 Only "Analytical Reagent Grade" (AR) or American Chemical Society (ACS) grade chemicals should be used.

7.3 Reagents may contain impurities, which can affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high-purity reagents must be used whenever possible. All acids must be ultra high purity grade. Redistilled acid is recommended. Nitric acid is preferred for ICP-MS order to minimize polyatomic interferences.

7.4 Nitric Acid, concentrated "Trace Metal" Fisher Scientific 500 mL in glass, catalog # A509-500 or "INSTRA-ANALYZED" Mallinckrodt-Baker, 500 mL in poly coated glass, catalog #9598-00

7.5 1:1 (vol/vol) nitric acid: Prepare by adding 50 mL concentrated nitric acid to 50 mL ASTM Type I water in a clean 125 mL HDPE bottle.

7.6 Tuning Solution: 10 µg/L Li, Ce, Y, Tl in 1% HNO_3.

7.7 Tune Check Solution stock: 10 mg/L Be, Mg, Co, In, Pb: NIST vendor purchased standard.

7.8 Tune Check Solution: 10 µg/L of Be, Mg, Co, In, and Pb: Prepare by pipetting 50 µL of Tune Check Stock solution into a 50 mL centrifuge tube, add 0.5 mL conc. nitric acid and bring to 50 mL total volume.

7.9 Internal Standard Stock Solution: 100 mg/L of Li, Sc, Y, In, and Tb and 1000 mg/L of Ge. Bismuth, as an internal standard, is not used as it is routinely found in environmental samples.

7.10 Internal Standard Working Solution for on-line addition of internal standards, (1 mg/L each element): Prepare by pipetting 0.5mL of Internal Standard Stock and 0.05 of the Internal Standard Stock containing Ge into a 50 mL centrifuge tube. Add 2.5 mL conc. nitric acid and bring to 50 mL total volume.

7.11 Multi-element Standard Stock Solutions: Mixes may be prepared from certified single-element solutions or purchased as mixes. If purchased as mixes, there is some danger of interferences from elements not on the list. For example, some mixes contain strontium, which can lead to incorrect calcium calibrations through an isobaric interference of doubly charged strontium on ^{43}Ca and ^{44}Ca. Care must also be taken to ensure that standard mixes do NOT contain any of the internal standard elements. All mixes should be prepared with high purity acids and ASTM Type I water using acid-cleaned, not previously used FEP fluorocarbon bottles for storage. Wherever possible, the use of glass should be avoided when preparing standards.

7.11.1 Calibration Stock A: 10 ppm of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Eu, Ho, Fe, La, Pb, Li, Mg, Mn, Mo, Ni, Se, Ag, Na, Sr, Tl, Th, U, V, Yb, Zn, and Bi. (in 2% HNO_3) + Trace HF - Purchased

7.11.2 Calibration Stock B: 10 ppm of Ag (in 1% HNO_3) - Not currently used.

7.11.3 Calibration Stock C: 1 ppm of Hg (in 1% HNO_3) - Not currently used.

7.11.4 Calibration Stock D: 100 ppm of Na, Ca, Mg, K, Fe (in 1% NHO_3) - Not currently used.

7.11.5 Calibration Stock E: 100 ppm of Au (in 2% HCl) - Not currently used.

7.12 QCS solution: The QCS must be obtained from a source independent of that used to prepare the calibration standards. It is used to check the validity of the initial calibration curves. It can be prepared exactly as the calibration standard mixes or purchased pre-prepared. Caution should be used if the QCS solution contains high concentrations of Sr which might interfere with analysis of Ca, see note in section on interference corrections.

7.13 Blanks: Four types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background, the rinse blank is used to flush the instrument between samples in order to reduce memory interferences and the field reagent blank is used to monitor field sampling problems.

7.13.1 Calibration Blank: 1% (v/v) nitric acid in ASTM Type I water

7.13.2 Laboratory Reagent Blank (LRB): Must contain all reagents in the same volumes as used in processing the samples. The LRB must be carried through the entire sample digestion and preparation scheme.

7.13.3 Rinse Blank: 3% (v/v) nitric acid in ASTM Type I water.

7.13.4 Field Reagent Blank (FRB): An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to all sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

7.14 Calibration Standards: Prepare fresh multi-element calibration standards weekly from the stock solutions as appropriate for analysis. All calibration standards are prepared in 50 mL polypropylene centrifuge tubes and brought to a final volume of 50 mL with 1% nitric acid in ASTM Type I water. The following calibration levels and ranges are appropriate for wide variety of samples.

Calibration Level	*1*	*2*	*3*	*4*	*5*	*6*	*7*
[trace elem.]	***0***	***1 ppb***	***10 ppb***	***100 ppb***	***0***	***0***	***0***
***[mercury1]**	***0***	***0***	***0***	***0***	***1 ppb***	***5 ppb***	***10 ppb***
***[major elem.]**	***0***	***100 ppb***	***1 ppm***	***10 ppm***	***0***	***0***	***0***
Vol. Cal A	0	500 µL, cal 4	50 µL	500 µL	0	0	0
***Vol Cal B**	0	50 µL	500 µL	2.5 mL	0	0	0
***Vol Cal C**	0	0	0	0	50 µL	250 µL	500 µL
***Vol Cal D**	0	50 µL	500 µL	5 mL	0	0	0
***Vol Cal E**[1]	50 µL	0	0	0	50 µL	50 µL	50 µL
Final Vol.	**50 mL**	**50 mL**	**50 mL**	**50 mL**	**50 mL**	**50 mL**	**50 mL**

Table 1: Preparation of calibration standard solutions from purchased multi-element calibration stock solutions.

***These Calibration Standards are not currently used.**

7.15. Calibration Tuning Solution: This solution is used to verify instrument tune and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (See 7.8) in 1% (v/v) nitric acid to produce a concentration of 10 µg/L of each element. Internal standards are not added to this solution.

7.16 Pulse to Analog (P/A) Calibration Solution: contains 100 ppb of all method analyte elements. Prepare by diluting a multi-element stock solution to 100 ppb (calibration standard # 4 may be used). To a 50 mL polypropylene centrifuge tube add 0.5 mL conc. nitric acid 500 µL of the 10 ppm stock solution and bring to 50 mL. This solution may be used for several months as long as the resulting P/A factors are consistent and in the range from 150 - 210.

7.17 10 µg/mL multi-element stock solutions used to spike LFM's and LFB's: Purchased Stock Standards are used.

[1] *IMPORTANT! Analysis of Hg requires the addition of 100 ppb of Au to all Standards, Blanks and Samples in order to stabilize the Hg. This should be done as soon after standard preparation or sample collection as possible to avoid loss of Hg.*

7.18 Sample Preservative, 20% nitric acid: one part concentrated nitric acid (reagent grade) is added to 4 parts reagent water. 5 mL of 20% solution is dispensed into plastic vials; one vial is added to 500 mL of sample.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Prior to sample collection, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration, acid preservation, etc., should be performed at the time of sample collection or as soon thereafter as practically possible.

NOTE: MATRIX MATCHING ACID CONCENTRATIONS AND COMPOSITIONS BETWEEN STANDARDS, BLANKS AND SAMPLES IS VERY IMPORTANT IN ICP-MS ANALYSIS.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. Glass or plastic filtering apparatus are recommended to avoid possible contamination. Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate to a pH < 2 with 20% nitric acid (5 mL per 500 mL of sample) immediately following filtration.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with 20% nitric acid (5 mL per 500 mL of sample) to pH < 2. Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, the samples may be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory.

8.4 Samples are collected in 500 mL plastic bottles for all total or dissolved metals except mercury. Samples for the SDWA copper-lead program are collected in 1 L bottles and are not preserved in the field. All samples are stored at room temperature prior to analysis.

8.5 All drinking water samples must be checked for turbidity and visually inspected for particulates. If turbidity is > 1.0 NTU or particulates are present, the sample must be digested prior to analysis. If no particulates are present and the turbidity is < 1.0 NTU, the sample does not require digestion before analysis. Record turbidity check in the computer.

8.6 When the sample is received in the laboratory, a pH check is done to verify that the sample has been preserved properly. Record this preservation check in the computer. If pH is not < 2, the sample is acidified with 1 mL concentrated nitric acid and the comment "Sample acidified in laboratory" entered into the computer.

NOTE: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.7 Following acidification in the laboratory, the sample should be mixed, held for 16 hours, and then verified to be pH < 2 just prior to withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be > 2, more acid must be added and the sample held for 16 hours until verified to be pH < 2.

8.8 If properly acid preserved, the sample can be held up to six months before analysis for all metals, except mercury.

8.9 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same type of container and acid preservative as used in sample collection.

8.10 Solid samples usually require no preservation prior to analysis other than storage at 4° C. There is no established holding time limit for solid samples.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability/Performance: The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to samples being analyzed by this method. The analyst must successfully complete the following:

9.1.1 Linear Calibration Ranges:

9.1.1.1 Calibrate the instrument as described in Section 10, and in the HP 4500 ChemStation Operators Manual section 9-2.

9.1.1.2 Run a series of standards at increasing concentrations beginning at 10 ppm at intervals of 5 ppm. Multi-element standard solutions should be used whenever possible.

9.1.1.3 The Upper Linear Dynamic Range is defined as the maximum concentration for each element for which the measured concentration is within 10 % of the actual value.

9.1.1.4 The current practice of the laboratory is to reanalyze all samples that are over the highest calibration standard, at a dilution.

9.1.2 External verification of calibration: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within ± 10 % of the established QCS value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limits (MDL) study: Method detection limits (MDL) are established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$MDL = (t) \times (S)$

where,

t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.14 for seven replicates).

S= Standard deviation of the replicate analyses.

MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.1.4 Analyze 4 replicate mid-level check standards containing each analyte of interest. For each analyte, calculate the measured concentration in each replicate, the mean concentration of the replicates, the mean accuracy (as a percentage of true value) and the precision (as relative standard deviation, RSD) of the measurements. The mean accuracy must be ± 20 % of the true value and the precision of the recovery (accuracy) must be <20% for each analyte. If these criteria are not met for an analyte of interest, take corrective action and repeat the measurements for that analyte until satisfactory performance is achieved. The spiking concentrations, recoveries, and percent relative standard deviations are on file in the MDH Environmental laboratory.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 External verification of calibration: Analyze a quality control sample (QCS) from the external source immediately after calibration to verify instrument performance. The results of the QCS must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.2 Demonstration of low background: At the beginning of the analytical run, analyze a laboratory reagent blank (LRB) to determine reagent or laboratory contamination. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. The background level of the analyte must be below the MDL, otherwise the source of the contamination is investigated and corrected and the samples are reanalyzed. With each batch of samples and at the end of the analytical run, analyze a continuing calibration blank (CCB).

9.2.3 Linear Dynamic Range: The Upper Linear Dynamic Range should be re-determined whenever one of the following occurs:

9.2.3.1 Six months has passed since last determination;

9.2.3.2 A new detector is installed; or,

9.2.3.3 The instrument is tuned for significantly different sensitivity

9.2.4 Continuing verification of calibration: Analyze the initial calibration verification (ICV) sample after calibration. Analyze a continuing calibration verification (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, the ICV or CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.5 Accuracy: At the start of an analytical run, analyze a laboratory fortified blank (LFB). The accuracy as percent recovery is calculated. If the recovery of any analyte falls outside the control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analysis. When sufficient internal performance data become available, develop control limits from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = X + 3S

LOWER CONTROL LIMIT = X - 3S

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent 20 to 30 data points.

9.2.6 Matrix effects: Run a laboratory fortified matrix (LFM) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The same solution used to fortify the LFB is used to fortify the LFM. Ideally for water samples, the analyte concentration should be the same as that used in the LFB. For solid samples, the concentration added should be 50 mg/kg equivalent (100 µg/L in the analysis solution). Over time, samples from all routine sample sources should be fortified. If recovery of any analyte falls outside the designated range, the LFM is repeated. If the recovery of the repeat analysis also falls outside these control limits, the possibility of matrix effects is investigated by immediately analyzing a LRB and LFB. If the recovery of the LFB for that analyte is within the control limits, then the recovery problem encountered with the LFM is considered to be matrix related, not system related and the analysis may continue provided that the CCV is within acceptable limits.

The result for that analyte in the unfortified sample must be labeled "suspect/matrix" to inform the data user that the results are suspect due to matrix effects.

9.2.6.1 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified samples, and compare these values to the control limits established in Section 9.2.5, for the analyses of LFB's. Recovery calculations are not required if the concentration of the analyte added is less than 10% of the samples background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{Cs - C}{S} \times 100$$

where,

R	=	percent recovery
Cs	=	fortified sample concentration
C	=	sample background concentration
S	=	concentration equivalent of fortifier added to sample

9.2.7 Precision: Analyze a laboratory duplicate (LD) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The absolute difference between duplicates and relative percent difference (RPD) of the duplicates are calculated and used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If the difference or RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.8 Internal Standard Responses:

9.2.8.1 The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard should not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than this are observed, use the following test procedure:

9.2.8.2 Flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two and reanalyze.

9.2.8.3 If test 9.2.8.2 above is not satisfied, or if it is a blank or calibration standard that is out of limits, terminate the analysis, and determine the cause of the drift. Possible causes of drift may be due to gradual accumulation of sample matrix on the interface (cones, extraction lenses) or a change in the state of tune of the instrument.

9.3 External verification of laboratory performance: Performance evaluation (PE) samples are analyzed as required for Federal certification. If the results are not within the control limits, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Leader, Program Manager and Laboratory Quality Assurance (QA) Officer.

9.4 Method detection limit (MDL) study: The MDL study is repeated annually or sooner if there is a change in analyst, or whenever a significant change in background or instrument response is expected or has occurred (ex. detector change). A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value of 2 to 5 times the estimated detection limit. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3) MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 QC Summary

9.5.1 Initial Demonstration of Performance

!	Establish MDLs	every twelve months [2]
!	Establish Linear Range	every six months [3]

9.5.2 Daily Demonstration of Performance

!	Tune	-	before beginning analyses
!	Tune Verification	-	beginning of run
!	Initial Calibration	-	beginning of run and when CCV fails
!	QCS	-	After calibration
!	CCV	-	beginning, end and after every 10 samples
!	LRB	-	each batch or 20 samples
!	LFB		each batch
!	LFS	-	each batch or 10 samples
!	LD1 and LD2	-	each batch or matrix type

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required periodically throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a calibration check is required at the beginning and end of each period during which analyses are performed, and at requisite intervals. Calibration must include a calibration blank and at least 1 additional calibration point for each element, which brackets the expected sample analyte concentration range. It is recommended that at least one calibration point for each detector mode (pulse or analog) be included for those elements, which are calibrated over a range which might include analog acquisition mode.

10.2 Initial calibration accuracy must be evaluated before any samples are analyzed through the analysis of a Quality Control Sample (QCS), which includes all analytes of interest. The QCS should be at or near the midpoint of the calibration range and must quantitate within 10% of the expected value.

---

[2] *MDLs and Linear Ranges must also be verified whenever system maintenance which may alter these values is performed such as detector replacement or significantly different tune parameters are set.*

[3] *Doubly-charged Strontium interferes with Calcium at m/z 43 and 44 the correction factor for $^{88}Sr++/^{88}Sr+$ must be determined daily or any time the tune conditions are changed.*

10.3 Calibration drift is monitored through the analysis of a Continuing Calibration Verification standard (CCV) at the beginning of the sample block, after every 10 samples and again at the end of samples. It must quantitate within 10% of expected value. If it is between 10% and 15%, the initial calibration must be re-done before additional samples can be analyzed. If it is > 15% out, the system must be recalibrated and the last 10 samples reanalyzed.

10.4 HP 4500 Tuning and Tune Verification

10.4.1 After initiating the plasma, allow the instrument to warm up while aspirating a blank solution for at least 15 minutes. During this warm-up, select ***Tune>> Sensitivity>> Start*** so that the instrument is scanning. After the 15-minute warm-up, aspirate the HP 4500 Tune Solution #1 (10 ppb Li, Y, Ce, Tl) and check for responses and RSDs. Generate and evaluate a tune report. The following are suggested guidelines for an acceptable tune for method 200.8

10.4.2 Suggested Tune Specifications:

Sensitivity:	Li	>5,000 cts/0.1 sec/10 ppb
	Y	>10,000 cts/0.1 sec/10 ppb
	Tl	>5,000 cts/0.1 sec/10 ppb
Precision:	Li	< 15 % RSD (0.1 sec integration time)
	Y	< 15% RSD (")
	Tl	< 15% RSD (")
Oxides:	< 1%	
Ce^{++}/Ce^{+}		< 5.0%
Background:	Li	< 30 cps
	Y	<15 cps
	Tl	< 15 cps
Mass Resolution:		W-10% 0.65-0.9 AMU
Mass Axis:		nominal mass +/- 0.1 AMU for ^{7}Li, ^{89}Y and ^{205}Tl

10.4.3 Tune Verification for method 200.8:

After warm-up and verification of instrument tune, compliance with method tune criteria must demonstrated. This is achieved by analyzing the 200.8 tune solution using the 200.8 tune method (2008tune.m).

Resolution at low mass is indicated by magnesium isotopes 24, 25, 26. Resolution at high mass is indicated by lead isotopes 206, 207, 208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass. Instrument stability must be demonstrated by running the tuning solution a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%. A tune compliance report will be automatically generated flagging any out of control results.

11.0 PROCEDURE

11.1 See the HP 4500 "ChemStation Operators Manual." Also see the current operating conditions in Appendix A, "Method Data Acquisition and Analysis Parameters."

11.2 Startup:

11.2.1 Verify argon supply and pressure.

11.2.2 Turn on water chiller and exhaust fan.

11.2.3 Insure that the internal standard solution bottle is adequately full (consumption is approximately 40 µL/min or 25 min/mL).

11.2.4 Verify contents of ALS rinse port reservoir(s).

11.2.5 Insure that the drain reservoir is not full.

11.2.6 Insure that all peristaltic pump tubes are in good condition and correctly clamped into the peristaltic pumps. Verify that the flow of sample and internal standard solutions through the uptake lines and into nebulizer is free from pulsations by introducing a bubble into each line and observing its progress.

11.2.7 Initiate the plasma and allow at least 15 minutes of warm-up while scanning the mass analyzer. The tuning procedures may then be carried out during the next 15 minutes of warm-up.

11.3 Tuning:

11.3.1 Verify the basic instrument tune as per section 10. Generate and file the tune report.

11.3.2 Aspirate a 100 ppb solution for all analyte elements and run P/A Autotune. File P/A report with tune report.

11.3.3 Aspirate a new rinse blank for 5-10 minutes to eliminate any carry-over into the calibration blank.

11.4 Sample Preparation

11.4.1 For preparation of sample tubes, see the "Preparation of Metals Labware" procedure.

11.4.2 For sample digestion requirements and details of sample preparation, see the Sample Preparation SOP.

11.4.3 The sample list may be created using the sequence autobuilder, imported from a LIMS system, or created in Excel. See the user's manual for the structure of the sample list if created outside the sequence autobuilder.

11.5 Sample dilutions: Dilute samples with reagent water that are greater than the linear range sample value (LRS) (10 mg/L).

11.6 Preparation of LFB and LFM: Add 25 µL of 10 µg/mL multi-element Stock Solutions to 5 mL of reagent blank or sample. The final concentration is 50 µg/L.

11.7 Automated Calibration, Quality Control and Sample Analysis:

11.7.1 Prepare calibration standards, blanks, spikes, samples, and QC samples as per Sections 7 and 8.

11.7.2 Autobuild a QC Sequence using sequence template.

11.7.3 Exit sequence autobuilder, and print the vial position guide.

11.7.4 Make any changes to the newly created sequence such as editing the sample types for spikes and spike reference samples.

11.7.5 Save the new sequence.

11.7.6 Sample Trays

11.7.6.1 Non-digested samples: invert 2-3 times then transfer ~5 mL directly into 14 mL sample tubes.

11.7.6.2 Digested samples: Pipet 5 mL of sample from 50 mL digest vial to 14 mL sample tube. (Do not shake digest vial prior to pipetting)

11.7.7 Load the autosampler according to the vial position guide.

11.7.8 Load the method tune2008.m.

- Run the tune2008.m method on the tune check sample, including data acquisition and data analysis. The 200.8 tune report will be generated.
- If desired, the CLP-style tune report may also be generated from ***Data Analysis >> Spectrum >> Generate Tune Report***

11.7.9 Select ***Sequence >> Run***

11.8 Instrument Shut Down

11.8.1 The instrument can be programmed for automated shutdown as well as manual shutdown.

11.8.2 When you finish running samples for the day, turn off plasma and return the instrument to **STANDBY** mode. To turn off the plasma, complete the following steps:

1. ***Select Top >> Instrument***
   The instrument menu appears

2. ***Select Instrument >> Instrument Control***
   The instrument control window appears showing the instrument control diagram. The window title bar indicates that the instrument is in **ANALYSIS** mode.

3. ***Select Plasma >> Plasma Off***
   A dialog box appears, asking if you want to turn the plasma off.

4. ***Click Yes***
   The plasma will turn off. The plasma on the instrument control diagram will disappear, and the HP 4500 will change from **ANALYSIS** mode to **STANDBY** mode.

5. Loosen the peristaltic pump clamps and release the tension on the tubing.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 All calculations necessary to convert raw spectral intensity data into quantitative results are performed by the Agilent 4500 ChemStation software.

12.2 Calibration blank subtraction, as required by method 200.8 is achieved by the use of the y=ax+b curve fit. In this manner, the internal standard signals are not subtracted from any sample or standard

12.3 Any additional dilutions not accounted for in the normal sample prep, which were entered in the sample log, table of sequencing will be corrected for by the ChemStation software.

ORIGINAL

Controlled Copy
3

12.4 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

12.5 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

12.6 After completion of the sequence, the Sequence QC Summary Report should be printed and used to help evaluate any QC problems. Select ***Sequence >> View Sequence >> Summary Report***

12.7 The method detection limit (MDL) for each analyte is calculated as described in 9.4. The current MDL values are on file.

12.8 The minimum report level for each analyte is on file.

12.9 Raw results are transferred to the LIMS and final results are reported in µg/L to 3 significant figures.

12.10 Direct data transfer is used to enter data into LIMS.

12.11 The average concentration of any laboratory duplicate analysis is reported.

12.12 If an MCL level is exceeded, the LIMS system automatically notifies Drinking Water Program.

12.13 Automatic Data transfer: Data is reviewed from hard copy before transferring file to work form where it is further reviewed and quality control checked. Any necessary editing is made before sending to database. Sample results, duplicates, spikes, standards, and blanks are sent to the database together.

12.14 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 METHOD PERFORMANCE

13.1 Information pertinent to our laboratory's performance can be found in our Quality Assurance Manual, Section 9.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures see Public Health Laboratory Hazardous Waste Manual, DRAFT, October 1994.

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reclamation, recycling and purchasing.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.

- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 Follow the procedures below to avoid exposure to the contents of the drain vessel:

15.2.1 Use the capped plastic drain vessel provided with the instrument. Never use glass.

15.2.2 Place the drain vessel on the instrument table below the peristaltic pump, where it is easy to check the liquid level.

15.2.3 Check the drain vessel frequently. Empty it before you ignite the plasma. The drain vessel will be full if you run the HP 4500 with the ASX 500 autosampler for more than 10 hours.

15.2.4 Be aware of the nature of the vessel contents. If the contents are toxic, dispose of them as hazardous waste. Also, always empty the vessel when switching from aqueous to organic sample solutions.

15.3 Samples containing hazardous levels of analytes should be flagged and disposed of properly.

15.4 For additional information regarding the laboratory's waste management policy, see Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

16.0 REFERENCES

16.1 "Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma – Mass Spectrometry," U.S. Environmental Protection Agency, Method 200.8, revision 5.4, 1994.

16.2 "Standard Methods for the Examination of Water and Wastewater," Method 3125B, 20th Edition 1998.

16.3 "Appendix B to Part 136 - Definition and Procedure for the Determination of Method Detection Limit - Revision 1.11," Federal Register, Vol. 49, No. 209, Friday, October 26, 1984, pp. 198-204.

16.4 "Standard Operating Procedure," EPA Method 200.8, ICP - MS, Agilent Technologies, Revision 1.5, 7/29/97.

16.5 "Determination of Trace Elements in Ambient Water by Inductively Coupled Plasma - Mass Spectrometry," U.S. Environmental Protection Agency, Method 1638, January 1996.

16.6 Operator's Manual, (Revision C), HP 4500, Agilent Technologies, July 1999.

16.7 "Sample Preparation for Spectrochemical Analysis of Total Recoverable Elements," MDH Method, 06-27-01.

17.0 DIAGRAMS, FLOWCHARTS, VALIDATION DATA

17.1 The initial Demonstration of Capability data is on file; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

ORIGINAL

Controlled Copy
3

S:\public\methods\sops.final-2000\200.8Revb.03.30.04.doc

Developed By: Robert Class Date: 04-01-00

Written By: Robert Class/Keith Peacock Date: 07-12-01

Revised By: Robert C. Class Date: 04-13-04

Approved By: Jeffrey Brenner (Unit Leader) Date: 04-13-04

Reviewed By: William H. Date: 04-13-04
(QA Officer)

Approved By: Jean Kahilainen Date: 4-13-04
(Program Manager)

APPENDIX A

HP 4500 ICP-MS METHOD DATA ACQUISITION AND ANALYSIS PARAMETERS

I. Method Data Acquisition Parameters:

1.0 See the HP 4500 ChemStation Operators manual for detailed instructions on setting up the following conditions. These conditions are supplied with the HP Standard Operating Procedure, but should not be used for the analysis of samples without validation of performance under actual operating conditions.

2.0 Interference Equations:

2.1 The following interference equations are used to correct for isobaric elemental and polyatomic interferences. All equations must be specified in the ChemStation method before any other data acquisition or data analysis parameters are set.

Ca[4]	(1.000)(44C)-(0.0271)(88C)
V	(1.000)(51C)-(3.127)(53C)+(0.353)(52C)
As	(1.000)(75C)-(3.127)(77C)+(2.736)(82C)-(2.760)(83C)
Mo	(1.000)(98C)-(0.146)(99C)
Cd	(1.000)(111C)-(1.073)(108C)+(0.764)(106C)
In	(1.000)(115C)-(0.016)(118C)
Pb	(1.000)(208C)+(1.000)(207C)+(1.000)(206C)

Table A1: Recommended Elemental Interference Equations

[4] *Doubly-charged Strontium interferes with Calcium at m/z 43 and 44 the correction factor for $^{88}Sr^{++}/^{88}Sr^{+}$ must be determined daily or any time the tune conditions are changed.*

3.0 Acquisition Mode: Spectrum

Points per Mass: 3
Number Replicates: 3
Integration Time: 0.1 sec for all elements except As, Se, Cd, Hg and their correction masses.
0.3 sec for As, Se, Cd and associated correction masses
1.0 sec for Hg

4.0 Peristaltic Pump Program:

Uptake speed: 0.3 rps
Uptake time: 60 sec [5]
Stabilization Time: 50 sec
Rinse Port Speed: 0.3 RPS
Rinse Port Time: 5 sec (after standards and samples)
Optional Rinse Speed: 0.3 rps
Optional Rinse Time: 60 sec [6]

5.0 Acquisition Masses:

			Integration	Time
Mass	Element	Det. Mode	per point	per mass
9	Be	Auto	0.1000	0.3000
27	Al	Auto	0.1000	0.3000
45	Sc	Auto	0.1000	0.3000
51	V	Auto	0.1000	0.3000
52	(V)	Auto	0.1000	0.3000
60	Ni	Auto	0.1000	0.3000
62	Ni	Auto	0.1000	0.3000
63	Cu	Auto	0.1000	0.3000

Table A2: Acquisition masses for each element with recommended integration times

[5] *IMPORTANT! Analysis of Hg requires the addition of 100 ppb of Au to all Standards, Blanks and Samples in order to stabilize the Hg. This should be done as soon after standard preparation or sample collection as possible to avoid loss of Hg.*

[6] *Sample uptake time and optional rinse time may be increased or decreased depending on the washout time of the sample tube and the complexity of the sample matrix.*

Mass	Element	Det. Mode	Integration per point	Time per mass
65	Cu	Auto	0.1000	0.3000
66	Zn	Auto	0.1000	0.3000
67	Zn	Auto	0.1000	0.3000
68	Zn	Auto	0.1000	0.3000
75	As	Auto	0.3000	0.9000
77	(As)	Auto	0.3000	0.9000
82	Se	Auto	0.3000	0.9000
83	(Se)	Auto	0.3000	0.9000
89	Y	Auto	0.1000	0.3000
95	Mo	Auto	0.1000	0.3000
97	Mo	Auto	0.1000	0.3000
98	Mo	Auto	0.1000	0.3000
99	Ru	Auto	0.1000	0.3000
105	Pd	Auto	0.1000	0.3000
107	Ag	Auto	0.1000	0.3000
108	(Cd)	Auto	0.3000	0.9000
109	Ag	Auto	0.1000	0.3000
111	Cd	Auto	0.3000	0.9000
114	Cd	Auto	0.3000	0.9000
115	In	Auto	0.1000	0.3000
118	Sn	Auto	0.1000	0.3000

Table A2: Acquisition masses for each element with recommended integration times

121	Sb	Auto	0.1000	0.300
123	Sb	Auto	0.1000	0.3000
135	Ba	Auto	0.1000	0.3000
137	Ba	Auto	0.1000	0.3000
159	Tb	Auto	0.1000	0.3000
202	Hg	Auto	1.0000	3.0000
203	Tl	Auto	0.1000	0.3000
205	Tl	Auto	0.1000	0.3000
206-208	Pb	Auto	0.1000	0.3000
209	Bi	Auto	0.1000	0.3000
232	Th	Auto	0.1000	0.3000
238	U	Auto	0.1000	0.3000

Table A2: Acquisition masses for each element with recommended integration times

II. HP 4500 ICP-MS Method Data Analysis Parameters:

1.0 Calibration Levels:

1.1 Blank

1.2 10 ppb for trace elements, 100 ppb for Na, K, Mg, Ca and Fe

1.3 100 ppb for trace elements, 1000 ppb for Na, K, Mg, Ca and Fe

1.4 500 ppb for trace elements, 10,000 ppb for Na, K, Mg, Ca and Fe

1.5 Internal standard concentrations are 50 ppb for all levels, all internal standards.

2.0 Internal Standard References:

Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this SOP for general applications, detail the use of five internal standards; ^{6}Li, Sc, Y, In, and Bi. Additional internal standards such as Tb, Ho or Ge may be used if results indicate the presence of one or more of the internal standard elements in the samples or if recoveries for certain elements such as Zn or Cd are poor in some matrices. Internal standards must be present in all samples, standards and blanks at identical levels. This is achieved by directly adding the internal standard stock solution (1.0 ppm in 1% HNO3) to all samples, standards and blanks by on-line addition prior to nebulization using a second channel of the peristaltic pump and a mixing Y-connector. The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. A final concentration at the nebulizer of approximately 50 ppb will result from the addition of a 1 ppm solution.

2.1 The following internal standard references are recommended:

ISTD	Analytes
^{6}Li	Be
Sc	Na – Fe
Y	Co – Ag
In	Cd – Ba
Bi	Tl – U

Table A3: Recommended Internal Standards and Associated Elements

3.0 Calibration Curve Fits:

3.1 All quantitation masses.....y = ax+(blank)

All internal standard masses.....(excluded)

All interference correction masses.....(excluded)

All monitor masses (not for quant).....(excluded

4.0 Reporting Parameters:

4.1 QC Reports.....On - printer
All Other Reports.....Off

4.2 QC Criteria for Smart Sequencing and EnviroQuant reports:
See Attached QC Database Printout (Appendix 2).

PROCEDURE FOR THE DETERMINATION OF:

NITRATE + NITRITE NITROGEN IN WATER BY FLOW INJECTION ANALYSIS

Total Nitrate + Nitrite Nitrogen - 69
Dissolved Nitrate + Nitrite Nitrogen - 78

1.0 SCOPE AND APPLICATION

1.1 Nitrates occur in trace amounts in surface water and in fresh domestic wastewater, but may reach concentrations as high as 50 mg/L (as N) in the effluent of nitrifying biological treatment plants. Nitrates are an essential nutrient for many photosynthetic autotrophs and, in some cases, have been identified as the growth limiting nutrient. Nitrates may also attain high levels in some groundwater. Nitrates in drinking water can contribute to an illness known as infant methemoglobinemia. A limit of 10 mg/L nitrate (as N) has been set for drinking water to prevent this disorder.

1.2 This Standard Operating Procedure (SOP) is applicable to the detection of nitrite and nitrate in drinking water, ground water, surface water and saline waters, domestic and industrial wastes and agricultural runoff.

1.3 This SOP can be used for sample analysis under the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

1.4 The laboratory is certified by the US EPA to use this SOP for sample analysis under the SDWA.

1.5 The Minnesota Department of Health Laboratory reports the nitrate + nitrite results as N to its clients.

1.6 The US EPA has established a drinking water MCL of 10.0 mg/L of nitrate as nitrogen.

1.7 The working range is 0.05 to 10.0 mg/L nitrate + nitrite nitrogen. Dilutions are prepared for concentrations greater than 10.0 mg/L.

1.8 All samples are verified to have a pH of 2.0 or less when received by the laboratory. While the reference method specifies that the pH of a sample is to be adjusted to between 5 and 9 with either concentrated hydrochloric acid (HCl) or concentrated ammonium hydroxide (NH_4OH), the pH is actually adjusted to between 5 and 9 with a high-ionic-strength ammonium chloride buffer at pH 8.5 (see Section 7.3). This step is accomplished in-line with the flow injection system before the sample enters the cadmium-reduction column. Supporting data generated by this laboratory show that the ammonium chloride buffer has sufficient buffering capacity to neutralize the acidified samples in line. These supporting data are on file with the Quality Assurance Officer.

1.9 Samples for dissolved nitrate + nitrite nitrogen are filtered through a 0.45 µm membrane filter at the time of collection or when received by the laboratory and prior to preservation. One filter blank should be run for each batch of ten samples.

1.10 This SOP is compliant with the requirements of EPA 353.2 except for adjusting of the pH of the sample with concentrated HCl or concentrated NH_4OH (see Section 1.8). The addition of the ammonium chloride buffer, pH 8.5, accomplishes this.

1.11 Storet Numbers:

Nitrate + Nitrite Nitrogen, Total	00630
Nitrate + Nitrite Nitrogen, Dissolved	00631

2.0 SUMMARY OF METHOD

2.1 This determination of nitrate plus nitrite utilizes an automated procedure in which nitrate is quantitatively reduced to nitrite by the passage of the sample through a copperized cadmium column. The nitrite ion (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride. This coupling forms a magenta colored azo dye which is measured colorimetrically at 520 nm on a Lachat QuikChem 8000 Flow Injection Ion Analyzer. Results are reported in mg/L as N.

2.2 The copperized cadmium column consists of cadmium granules treated with copper sulfate and packed in a glass column.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the Laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Reagent Blank (RB) immediately before any samples are analyzed and periodically throughout the run as needed.

4.2 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, turbid samples may be pre-filtered through a 0.45 µm pore diameter membrane filter.

4.3 Low results might be obtained for samples that contain high concentrations of iron, copper, or other metals. EDTA is added to the buffer to eliminate this interference.

4.4 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is mitigated by diluting the sample before analysis. Column efficiency is verified daily by a column efficiency check after the calibration and after every ten samples with the analysis of the CCV.

4.5 Residual chlorine can interfere by oxidizing the cadmium column which reduces its efficiency. If a chlorine smell is noticed after the sample bottle is opened, the sample should be diluted prior to analysis or rejected for analysis. Samples are not treated with sodium thiosulfate as this chemical reduces the efficiency of the cadmium column. Column efficiency is verified daily by a column efficiency check after the calibration and after every ten samples with the analysis of the CCV.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this method has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02	Occupational Safety and Health
420.01	Right-to-Know

In addition, the analyst should read the MDH Public Health Laboratory Division - Chemical Hygiene Plan. Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Safety Officer.

5.3 Safety glasses must be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.4 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.5. The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.5.1. Cadmium
5.5.2. Phosphoric acid
5.5.3. Hydrochloric acid
5.5.4. Sodium hydroxide
5.5.5. Ammonium hydroxide
5.5.6. Sulfanilamide
5.5.7. N-(1-naphthyl) ethylenediamine dihydrochloride (NED)
5.5.8. Sulfuric acid
5.5.9. Chloroform

5.6 Safety glasses, gloves and protective clothing should be worn when handling the chemicals listed above, and must be worn when handling cadmium in particular.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipets are Class A. All non disposable glassware must be rinsed with 1:1 HCl followed by 3 rinses with reagent water prior to use.

6.3 Lachat QuikChem 8000 Automated Flow Injection Ion Analyzer

6.3.1 Autosampler

6.3.2 Proportioning Pump

6.3.3 Injection Module with a microloop sample loop

6.3.4 Colorimeter

6.3.4.1 Interference Filter: 520 nm

6.3.4.2 Flow Cell: 10 nm, 80µl

6.3.5 Reaction Module 10-107-04-1-0 with Cadmium Column part number 50237A

6.3.6 3.0 Omnion Software System

6.4 13 x 100 mm disposable borosilicate glass tubes

6.5 Fixed and adjustable pipettes.

6.6 Pall Gelman IC Acrodisc 0.45µm Syringe Filters (PN4485) is used for dissolved analysis. These filters require no pretreatment.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with a resistivity > 16 megohm-cm at 25° C. and free of nitrate or nitrite.

7.2 Only "Analytical Reagent Grade" (AR) or American Chemical Society (ACS) grade chemicals should be used.

7.3 Ammonium Chloride Buffer: **CAUTION: Fumes!** In a hood, to a 2 L acid-rinsed volumetric flask, add 1000 mL reagent water, 210 mL concentrated hydrochloric acid (HCl), 190 mL of 28 – 30% ammonium hydroxide (NH_4OH), and 2.0 g disodium EDTA. Dissolve and dilute to the mark. Invert to mix. Adjust to pH 8.5 with concentrated HCl or 15 N sodium hydroxide (NaOH). Store in a plastic bottle.

7.4 Sulfanilamide Color Reagent: In an acid-rinsed 1 liter volumetric flask, add approximately 600 mL distilled water and a large stir bar. Then add 100 mL of 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 2.0 g N-1-naphthylethylenediamine dihydrochloride (NED). Stir to dissolve for 30 minutes. Remove stir bar, dilute to the mark, and invert at least 3 times to mix. Store the solution in an amber bottle and keep in the dark when not in use. The solution is stable for one month.

7.5 Cadmium-Copper Reduction Column: Purchase columns from Lachat, part number 50237A.

7.6 Standard preparation is recorded in the Standards Log Book. This includes stock, intermediate, and working standards. Use the previous record as a template.

7.7 Nitrate Stock Standard (1000 mg/L): In an acid-rinsed 1 liter volumetric flask, dissolve 7.218 g potassium nitrate (KNO_3), which has been dried in an oven at 105° C. for one hour in approximately 600 mL reagent water. Dilute to the mark and invert at least 3 times. Add 2 mL of chloroform to preserve. This solution is stable for 6 months.

7.8 Nitrite Stock Standard (1000 mg/L): In an acid rinsed 250 mL volumetric flask, dissolve 1.5175 g potassium nitrite (KNO_2) in approximately 150 mL reagent water. Dilute to the mark and invert at least 3 times. Add 0.5 mL of Chloroform to preserve. Store at 4°C.

7.9 Nitrate Working Standards

7.9.2 0.50, 1.0, 5.0, and 10.0 mg/L Working Standards: In acid-rinsed 200 mL volumetric flasks, add 4 mL of 10% H_2SO_4 (purchased commercially) in approximately 100 mL reagent water. Then add appropriate amount of 1000 mg/L Stock Nitrate Standard (Section 7.7) and dilute to mark with reagent water.

Standard Concentration mg/L	**1000 mg/L Stock Standard (Section 7.7)**
0.50	0.10 mL
1.0	0.20 mL
5.0*	1.0 mL
10.0	2.0 mL

Mix and pour into an acid rinsed 300 mL bottle, label and store at room temperature. Remake monthly.

*Prepare two bottles of 5.0 mg/L Std.

7.9.2 0.0, 0.05, and 0.10 mg/L Working Standards: In acid-rinsed 200 mL volumetric flasks, add 4 mL of 10% H_2SO_4 in approximately 100 mL reagent water. Then add appropriate amount of 10 mg/L intermediate standard shown below and dilute to mark with reagent water.

Standard Concentration mg/L	**10 mg/L Working Standard (from Section 7.9.1)**
0.0	0.0 mL
0.05	1.0 mL
0.10	2.0 mL

Mix and pour into an acid rinsed 300 mL bottle, label and store at room temperature. Remake monthly.

7.10 Column Efficiency Check Standard

7.10.1 5.0 mg/L Nitrate Efficiency Standard: In an acid-rinsed 100 mL volumetric flask, add 0.5 mL of 1000 mg/L stock Nitrate standard. Dilute to mark with reagent water. Invert at least 3 times to mix. Make up fresh with each new run.

7.10.2 5.0 mg/L Nitrite Efficiency Standard: In an acid-rinsed 100 mL volumetric flask, add 0.5 mL of 1000 mg/L stock Nitrite standard. Dilute to mark with reagent water. Invert at least three times to mix. Make up fresh with each run.

7.11 1:1 HCl

7.12 All reagents should be discarded if precipitate of growth appears.

7.13 All reagents and standards are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 SDWA Samples

8.1.1 Samples are collected in 175 mL plastic bottles containing 3.5 mL 10% H_2SO_4 preservative.

8.1.2 Samples are stored at 4°C.

8.1.3 Maximum holding time is 14 days.

8.2 CWA and Other Non-MDH Samples

8.2.1 Samples are collected in 250 mL plastic bottles.

8.2.2 Samples are preserved at the time of collection by the addition of 5 mL 10% H_2SO_4.

8.2.3 Samples are stored at 4°C.

8.2.4 Maximum holding time is 28 days.

8.3 Non-Compliance Drinking Water Samples

8.3.1 Samples are collected in 125 mL bottles.

8.3.2 Samples are preserved in laboratory with 10% H_2SO_4 preservative. Samples may not contain sodium thiosulfate since it reduces life of cadmium column.

8.3.3 Samples are stored at 4°C.

8.3.4 Maximum holding time for non-compliance samples is seven days.

8.4 When the sample is received in the laboratory, a pH check is done to verify that the sample has been preserved properly. Record this preservation check in the computer. If pH is not ≤ 2, the sample is acidified with 10% H_2SO_4 preservative and the comment "Sample acidified in laboratory" entered into the computer.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability: The analyst must make an initial demonstration of capability to generate acceptable accuracy and precision data with this method by successful completion of the following:

9.1.1 Initial calibration: The linear calibration range (LCR) must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument. Acceptable correlation coefficient for the calibration is 0.995 or greater. Determined concentration for high level standards should be ± 10% of the true value and ± 20% of the true value for low level standards. This corresponds to the % residual calculation.

9.1.2 External verification of calibration: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within ± 10% of the established QCS value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method detection limit (MDL) study: A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.1.4 Initial precision and accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily calibration: Calibrate the instrument with a calibration blank and at least 3 calibration standards covering the range of sample results and within the linear calibration (LCR) of the analyte. The curve used must be linear and not forced through zero. Acceptable correlation coefficient for the calibration curve is 0.995 or greater. The concentration of the calibration standards should be ± 10% of the true value, and ± 20% of the true value for lowest standard. This corresponds to the % residual calculation. The Calibration Statistics display on the analysis report summarizes in algebraic form what is seen graphically. The first equation shows the plotted calibration equation in the form of **Area = f (Conc)**, where the peak area is a function of the **Conc** or determined concentration of the analyte. The second equation is the same calibration equation, but solved for concentration. It is in the form **CONC = f (Area)**. This is the equation that is used to determine the concentration of unknowns. The third statistic is the value of **r**, the 'correlation coefficient' for the calibration.

9.2.2 External verification of calibration: Analyze a quality control sample (QCS) from the external source immediately after calibration to verify instrument performance. The results of the QCS must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.3 Demonstration of low background: At the beginning of the analytical run, analyze an initial calibration blank (ICB), or a laboratory reagent blank (LRB) to determine reagent or laboratory contamination. The background level of the analyte must be below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed. With each batch of samples and at the end of the analytical run, analyze continuing calibration blanks (CCBs). The value of the CCB must be below the Report Limit for the run to continue. If the CCB is above the Report Limit of 0.05 mg/L, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Continuing verification of calibration: Analyze the initial calibration verification (ICV) sample after calibration. Analyze continuing calibration verification (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, the ICV or CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.5 Accuracy: At the start of an analytical run, analyze a laboratory fortified blank (LFB). The accuracy as percent recovery is calculated. If the recovery of the analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analysis.

9.2.6 Matrix effects: Run a laboratory fortified matrix (LFM) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The same solution used to fortify the LFB is used to fortify the LFM. The accuracy, as percent recovery after background correction, is calculated. If the recovery of the LFM falls outside of 90-110% limits, the LFM is repeated. If the recovery of the repeat analysis also falls outside these control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the LFM of the diluted sample is within the control limits, then the recovery problem encountered with the LFM is considered to be matrix related, not system related, and the analysis may continue provided that the CCV is within acceptable limits. The diluted sample result is reported with an elevated report level reflective of the dilution used and the following remark code (DM) is added: "Report Level was changed due to matrix interference." If the recovery of the LFM from the diluted sample falls outside the acceptable limits, the result is reported using an elevated report level reflective of the dilution used and the following comment is added: "Spike recovery was xx%".

9.2.7 Precision: Analyze a laboratory duplicate (LD) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The absolute difference between duplicates and relative percent difference (RPD) of the duplicates are calculated and used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If the difference or RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.8 Column Efficiency Check: Two 5.0 mg/L Nitrate Standards and two 5.0 mg/L Nitrite Standards are analyzed at the beginning of each run to determine the efficiency of the cadmium column (NO_3/NO_2) x 100 = % column efficiency. If the efficiency falls outside the required control limits of 90-110%, the column should be replaced. Record the determined % column efficiency in the instrument QC Manual.

9.3 External verification of laboratory performance: Performance evaluation (PE) samples are analyzed as required for Federal certification. If the results are not within the control limits, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Leader and Laboratory Quality Assurance (QA) Officer.

9.4 The MDL study is repeated annually, or when changes in analyst, instrumentation or instrument response occur. A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit and, ideally analyzed over a period of at least 3 days. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B (see Section 16.3). MDLs must be low enough for regulatory/client purposes; otherwise remedial action is taken and the process is repeated.

9.5 Dissolved Analysis: The filtration blank results must be below the report limit. If the filter blank is above the report limit, consult with a lead worker or supervisor to determine if the filter blank result should be subtracted from the sample result or if other action should be taken.

9.6 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of QCS, LFB, CCV, and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 6 calibration standards and a calibration blank by diluting suitable volumes of calibration standard solution, as describe in Section 7.10.

10.2 Process calibration standards and calibration blank as described in Section 11. Additionally, refer to Lachat manual for the operation of the instrument.

10.3 Read calibration standards and calibration blank in descending concentration on the Lachat 8000.

10.4 Prepare the calibration standard curve by plotting instrument response against concentration values. The curve fir must be linear and not forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the Omnion 3.0 software. Acceptable correlation coefficients are 0.9950 or greater. A curve is accepted if the calibration standards are within 10% of the true value except for the lowest non-zero standard, which can deviate by 20%. Print a copy of the curve to document the initial calibration.

10.5 After the calibration has been established, it must be verified by the analysis of a laboratory reagent blank (LRB), laboratory fortified blank (LFB) and a suitable quality control sample (QCS). If measurements exceed ± 10% of the established LFB or QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis. A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) should be run every 10 samples and at the end of each run. The result for the LRB must be less than or equal to the calculated MDL and the result for the CCB must be less than on equal to 0.05 mg/L. The results for the calibration verification standard (CCV) must be within ± 10% of the true value (5.0 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. Samples following the last acceptable CCV and CCB are reanalyzed.

10.6 The cadmium column must have column efficiency from 90% to 100% before analyzing samples. See Section 9.2.8 for the procedure and to verify column efficiency.

10.7 Print calibration statistics when calibration is complete.

11.0 PROCEDURE

11.1 Prepare reagents and standards as described in Section 7.0 and use the manifold set up as shown in Section 17.2.

11.2 System Start-Up.

11.2.1 Inspect manifold for proper connections.

11.2.2 Turn on power strip.

11.2.3 Raise tension levers on pump tube cassettes. Place transmission lines into proper containers.

11.2.4 Allow reagents to pump through the system.

11.2.5 Place the cadmium reduction column on line by switching the two-state valve to the open position after reagents have been pumping through the system for 5 minutes. **Note: DO NOT LET AIR OR RINSE WATER ENTER THE COLUMN.**

11.2.6 Establish a stable baseline.

11.3 Select the default nitrate + nitrite run from the nitrate + nitrite data folder and input the information required by the data system, i.e. sample numbers, duplicates, and LFM's.

11.3.1 QC samples should be set up initially as follows:

1 Blank (LRB)
2 5.0 mg/L Nitrite standards
2 5.0 mg/L Nitrate standards
1 External Reference (QCS)
1 Laboratory Fortified Blank (blank spike), TV= 5.0 mg/L

11.4 Place standards in descending order in the auto sampler.

11.5 Pour samples into labeled test tubes and place into the sample trays(s).

11.6 Duplicates, LFM, CCV, and CCB are analyzed every 10 samples.

11.7 To prepare LFB and LFM add 25 µl of 1000 mg/L Nitrate Stock Standard (Section 7.7) to a test tube, add 5 mL of reagent water or sample, and vortex to mix. The True Value is 5.0 mg/L.

11.8 Calibrate the instrument by injecting standards. The data system will then associate the concentration with responses for each standard and evaluate the curve.

11.9 After acceptable curve and the initial QC shown is Section 11.4.1 is run, continue analysis.

11.10 System Shutdown

11.10.1 Take the cadmium reduction column off line by closing the two-state switching valve. **Note: DO NOT LET AIR OR RINSE WATER ENTER THE COLUMN.**

11.10.2 Place the transmission lines in water and flush system for 5 minutes. After 5 minutes remove transmission lines from water and pump manifold until dry (approximately 5 minutes).

11.10.3 Turn off pump, power, and release tension levers on pump tube cassettes.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calibration is accomplished by injection standards. The data system will then prepare a calibration curve by plotting instrument response versus standard concentration. Sample concentration is calculated from the regression equation. Multiply results by appropriate dilution factor.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file.

12.3 The minimum report level is 0.05 mg/L as N.

12.4 Results are reported as $NO_3 + NO_2$ in mg/L as N to two significant figures.

12.5 Laboratory duplicates, LFB and LFM are highlighted. QCS and CCV's are circled. The results are entered into the LIMS.

12.6 The average concentration of any laboratory duplicate analysis is reported.

12.7 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 10.0 mg/L are diluted and reanalyzed.

12.8 Subtract the concentration value for any color blanks from their respective sample result to correct for sample color or turbidity.

12.9 If the MCL of 10.0 mg/L is exceeded, the analyst notes this on the raw data printout and notifies the Public Water Supply Section within 24 hours following Unit procedures.

12.10 For a PWS sample, the LIMS will generate nitrate + nitrite data from previous samples taken at that location. This printout is reviewed by the Unit Supervisor or designee.

12.11 Results reports are reviewed by Unit Supervisor or designee according to established procedures prior to transmittal to client.

13.0 METHOD PERFORMANCE

13.1 Information pertinent to our laboratory's performance can be found in our Quality Assurance Manual, Section 9.

13.2 Current MDL data is available from the QA Officer.

13.3 Precision and accuracy data used for single laboratory testing will be summarized annually by the QA Officer.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures see Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reclamation, recycling and purchasing.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 All reagents (except cadmium), samples and process waste can be dumped down the sink. Spent cadmium columns are emptied into suitable waste storage container and disposed of by the Hazardous Waste Officer.

15.3 For additional information regarding the laboratory's waste management policy, see Public Health Laboratory Hazardous Waste Manual, DRAFT, October, 1994.

16.0 BIBLIOGRAPHY

16.1 "Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry," "Methods for the Determination of Inorganic Substances in Environmental Samples," EMSL-EPA, EPA/600/R-93/100, Method 353.2, Revision 2.0, August, 1993.

16.2 "Appendix B to Part 136 - Definition and Procedure for the Determination of Method Detection Limit - Revision 1.11," Federal Register, Vol. 49, No. 209, Friday, October 26, 1984, pp. 198-204.

16.3 Standard Methods for the Examination of Water and Wastewater, Method 4500-NO_3-F, Method 4500-NO3-I, 20th Edition, 1998.

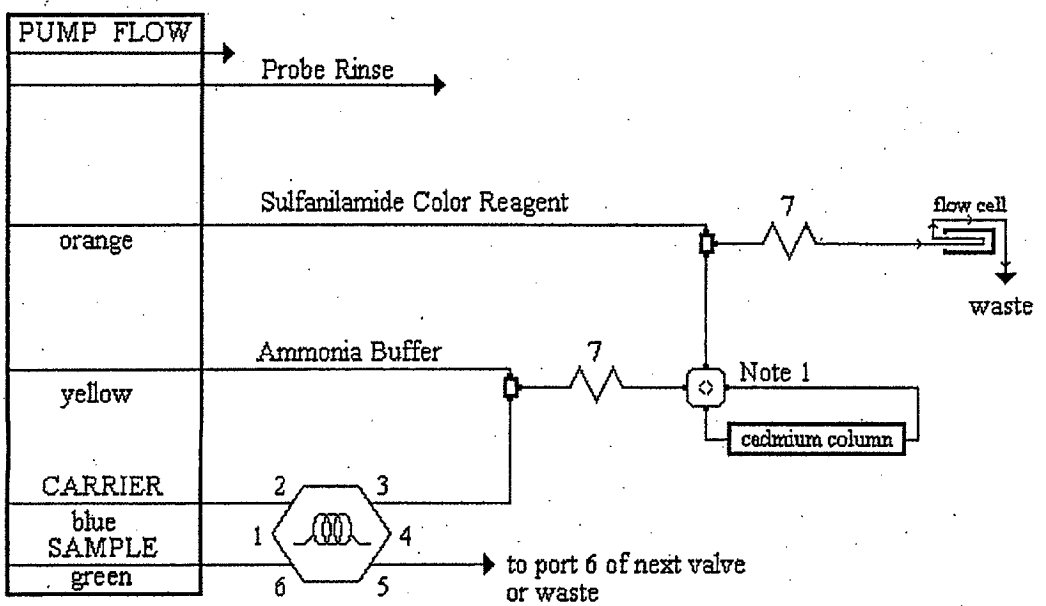
16.4 QuikChem Methods Manual. QuikChem Method Number Method 10-107-04-1-O. Revision date: 18 December 2000.

16.5 "Annual Book of ASTM Standards," Vol. 11.01, Method D3867-90(A), 1996.

17.0 DIAGRAMS, FLOWCHARTS, VALIDATION DATA

17.1 The initial Demonstration of Capability data is on file; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

17.2 Manifold Diagram - QuikChem 8000:

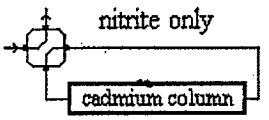


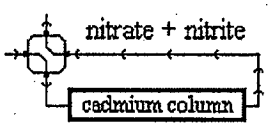
Carrier: **Helium degassed DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000 Sample Loop: 15 cm of **0.5 mm (0.022 in) i.d.** tubing. This is **2.5 µL/cm.**
Interference Filter: 520 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

7: **135 cm** of tubing on a 7 cm coil support

Note 1: This is a 2 state switching valve used to place the cadmium column in-line with the manifold.





17.3 QuikChem 8000

17.3.1 The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	60 samples/hour, 60 seconds/sample
Pump speed	35
Cycle Period:	60

17.3.2 Analyte Data:

Concentration Units:	mg of N/L
Expected Inject to Peak Start	12 seconds
Expected Peak Base Width	23 seconds
Chemistry:	Direct

17.3.3 Calibration Data:

Level	1	2	3	4	5	6	7	8
Concentration mg/L	10.0	5.00	2.00	1.0	0.5	0.10	0.05	0.0

Calibration Fit Type:	1st Order Polynomial
Calibration Rep. Handling:	Average
Weighting Method:	1/x
Concentration Scaling:	None
Force through Zero:	No

17.3.4 Sampler Timing:

Min. Probe in Wash Period:	9.0 seconds
Sample Period:	40.0 seconds

17.3.5 Valve Timing:

Load Period:	20 seconds
Inject Period:	40 seconds
Time to Valve	26 seconds

Developed By: Paul Bergh Date: 2-01-95

Written By: Mary Sobota & Elisabeth Dankert Date: 3-27-01

Revised By: Elisabeth Dankert Date: 5/24/05

Approved By: Keith Peacock Date: 5-24-05
Keith Peacock, BactiChem Unit Supervisor

Reviewed By: William Scruton Date: 5-24-05
William Scruton, QA Officer

Approved By: Louise W Liao Date: 5.26.05
Louise Liao, Env Lab Section Manager

Approved By: [signature] Date: 5-27-05
Norman Crouch, PHL Division Director

Erratum
Change in Progress Attachment

Notification Date: 6/22/05
Effective Date: 6/17/05

SOP Document Number: Nitrate + Nitrite – FIA-Water; Revision H, 5-12-05

SOP Description: Analysis of Nitrate + Nitrite by cadmium reduction, Flow Injection Analysis

The following change has been made to the referred SOP and will be included in the next revision of the SOP:

1.10 This SOP is compliant with the requirements of EPA 353.2 except for:

1.10.1 Adjusting of the pH of the sample with concentrated HCl or concentrated NH_4OH (see Section 1.8). The addition of the ammonium chloride buffer, pH 8.5, accomplishes this.

1.10.2 The sulfanilamide color reagent is prepared with 1.0 g instead of 2.0 g of N-1-naphthylethylenediamine dihydrochloride (NED). This change was implemented to avoid: 1) staining of mixing coils; 2) precipitation of reagent, 3) multiple clogs of reagent lines; and 4) multiple QC failures with initial QC (curve and per cent residuals), CCVs, and LFMs. Switching to 1.0 g (as recommended by Lachat SOP) has eliminated these problems.

7.4 . . . Then add 100 mL of 85% phosphoric acid (H_3PO_4), 40.0 g sulfanilamide, and 1.0 g N-1-naphthylethylenediamine dihydrochloride (NED). . . .

Approval Signatures — Date:

Nicole M.S. Trifilette — 8/11/05

Name/Title: Nicole Trifilette, Env. Analyst 1

Keith Peacock — 8-11-05

Name/Title: Keith Peacock, BactiChem Unit Supervisor

William Scruton — 8/12/05

Name/Title: William Scruton, Quality Assurance Officer

S:\public\methods\sops.final-2000\General Chemistry SOPs (Final)\UV_VIS_IR.030.F05.doc

PROCEDURE FOR THE DETERMINATION OF:

SILICA IN WATER

Molybdate-Reactive Silica - 30
Dissolved Molybdate-Reactive Silica - 50

1.0 SCOPE AND APPLICATION

1.1 Silica ranks next to oxygen in abundance and is a common constituent of igneous rocks, quartz and sand. Degradation of silica-containing rocks result in the presence of silica in natural waters as suspended particles, in a colloid or polymeric state, and as silica acids or silicate ions. Volcanic and geothermal heated waters often contain an abundance of silica. Concentrations of silica in natural waters are commonly in the range of 1 to 30 mg/L. Silica in water is undesirable for many industries, since it forms difficult to remove deposits on equipment, particularly high-pressure steam-turbine blades.

1.2 This Standard Operating Procedure (SOP) is applicable to the detection of silica in drinking, surface and saline waters, and domestic and industrial wastes.

1.3 This SOP can be used for sample analysis under the Safe Drinking Water Act (SDWA) and the Clean Water Act.

1.4 The laboratory is certified by the US EPA to use this SOP for sample analysis under the SDWA.

1.5 The working range of this method is 0.5 to 50 mg/L. Dilutions are prepared for concentrations greater than 50 mg/L. Working range of the reference method is 0.4 to 25 mg/L.

1.6 Samples for dissolved silica are filtered through a 0.45 µm membrane filter at the time of collection or when received by the laboratory. One filter blank should be run for each batch of ten samples.

1.7 This SOP is compliant with the requirements of:

Standard Methods, 20th Edition	4500-SiO_2 C

1.7.1 The oxalic acid solution is diluted to 100 mL. Standard Methods omits a final volume. This volume was derived from EPA Method 370.1 where 10 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) is diluted to 100 mL and 0.3 mL is added to 10 mL of sample. Standard Methods adds 0.4 mL of oxalic acid to 10 mL of sample. The two methods are equivalent if the oxalic acid is dihydrate rather than the monohydrate form listed in Standard Methods. The monohydrate form has not been found commercially available.

1.8 Storet Numbers:

Molybdate-Reactive Silica	00956
Molybdate-Reactive Silica, Dissolved	00955

2.0 SUMMARY OF METHOD

2.1 Ammonium molybdate, at approximately pH 1.2, reacts with silica and any phosphate present to produce heteropoly acids. Oxalic acid is added to destroy the molybdophosphoric acid that may have been formed. Even if phosphate is known to be absent, the addition of oxalic acid is mandatory because it decreases the interference from tannin. At least one form of silica does not react with molybdate. To analyze for this form, it must be converted to a reactive form by digesting the sample with sodium bicarbonate.

2.2 The heteropoly acids produce a yellow color whose intensity is proportional to the concentration of molybdate-reactive silica. The intensity is measured spectrophotometrically at 410 nm. Results are reported in mg/L as SiO_2.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the Laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Reagent Blank (RB) immediately before any samples are analyzed and periodically throughout the run as needed.

4.2 Because both apparatus and reagents may contribute silica, avoid using borosilicate glassware as much as possible, and use reagents low in silica.

4.3 Tannin, phosphates, large amounts of iron, color, turbidity and sulfide interfere with the analysis. Treatment with oxalic acid eliminates interference from phosphate and decreases interference from tannin. Use color blanks to cancel interference from color or turbidity.

4.4 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02	Occupational Safety and Health
420.01	Right-to-Know

In addition, the analyst should read the MDH Public Health Laboratory Division - Chemical Hygiene Plan. Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Safety Officer.

5.3 Safety glasses must be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.4 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.5 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.5.1 Hydrochloric Acid

5.5.2 Ammonium molybdate

5.5.3 Oxalic acid

5.5.4 Sodium metasilicate nonahydrate

5.6 Safety glasses, gloves and protective clothing should be worn when handling the chemicals listed above.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Lab ware - Wherever possible, lab ware should by polyethylene or polypropylene. Volumetric flasks and pipets are Class A.

6.3 Fixed and adjustable pipettes.

6.4 Beckman DU-640 spectrophotometer (or equivalent) equipped with 1 cm cell for use at 410 nm.

6.5 Vortex Mixer.

6.6 Polyethylene test tubes, 50 mL.

6.7 Pall Gelman IC Acrodisc 0.45 µm syringe filters (PN4485) are used for dissolved silica analysis. These filters require no pretreatment.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 megohm-cm at 25°C and free of the analyte silica.

7.2 Only Analytical Reagent (AR)-grade or American Chemical Society (ACS)-grade chemicals should be used.

7.3 All reagents should be stored in plastic containers.

7.4 1:1 HCl: Mix equal quantities of concentrated hydrochloric acid (HCl) with reagent water. Always add acid to water. Prepare in a fume hood.

7.5 Ammonium molybdate reagent: In a 100-mL volumetric flask, dissolve 10 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in reagent water by stirring and gently warming. Dilute to mark and adjust to pH to 7 to 8 with silica-free concentrated ammonium hydroxide (NH_4OH) or sodium hydroxide (NaOH). Store in plastic bottle.

7.6 Oxalic acid reagent: In a 100-mL volumetric flask, dissolve 7.5 g oxalic acid $(C_2H_2O_4\cdot 2H_2O)$ in reagent water and dilute to mark. Store in plastic bottle.

7.7 Stock Silica Standard (1000 mg/L): Purchased commercially available stock standard from Hach (order # 194-49) or an equivalent source.

7.8 Calibration Standards: To prepare 200-mL quantities of calibration standards, use a 200 mL volumetric flask. Fill the volumetric flask to the mark with reagent water and pour into a corresponding 250-mL plastic standard bottle. Repeat for each standard to be prepared. Remove the amount of reagent water shown in the table below and then add the corresponding amount of stock silica standard to the bottle. Invert to mix.

Calibration Standard Conc. mg/L	Quantity of reagent water to remove (mL)	Quantity of 1000 mg/L Stock Std (mL)
0.0	0.0	0.0
0.25 (MDL)	0.05	0.05
0.50	0.1	0.1
1.0	0.2	0.2
2.0	0.4	0.4
5.0	1.0	1.0
10.0	2.0	2.0
15.0	3.0	3.0
30.0	6.0	6.0
50.0	10.0	10.0

7.9 All reagents should be discarded if precipitate or growth appears.

7.10 All reagents and standards are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 SDWA samples are collected in 125-mL, 1-L or 2-L plastic bottles and stored at 4° C prior to analysis.

8.2 No preservatives should be added to the samples. The silica analyses cannot be performed on an acidified sample.

8.3 If dissolved analysis is requested and the sample has not been filtered in the field, the samples must be filtered upon arrival. Filter sample into a 125-mL plastic bottle and store at 4°C prior to analysis.

8.4 Glass containers should not be used because the silica in the glass may dissolve and contaminate the sample.

8.5 Samples are analyzed within 28 days of collection date.

8.6 Maximum holding time is 28 days when stored at 4° ± 2° C.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability: The analyst must make an initial demonstration of capability to generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial calibration: The linear calibration range (LCR) must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument.

9.1.2 External verification of calibration: A quality control sample (QCS) from an external source is analyzed. The results of the QCS must be within ± 10% of the established QCS value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method detection limit (MDL) study: A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.1.4 Initial precision and accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily calibration: Prepare the calibration standard curve by plotting instrument response against concentration values. A calibration curve will be fitted to the calibration standard concentration/response data using the instrument's computer. The curve is accepted if the standard deviation (SD) of the difference between the standards and their true values is ≤ 0.3 or a calibration coefficient of 0.9990 is achieved. Also, the concentrations of the calibration standards must be within ± 10% of the true value except for the lowest non-zero standard, which can deviate by ± 20%. Print a copy of the curve with the correlation coefficient to document the initial calibration. Write the SD on the calibration curve printout.

9.2.2 External verification of calibration: Analyze a quality control sample (QCS) from the external source immediately after calibration to verify instrument performance. The results of the QCS must be within ± 10% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.3 Demonstration of low background: At the beginning of the analytical run, analyze an initial calibration blank (ICB) or a laboratory reagent blank (LRB) to determine reagent or laboratory contamination. The background level of silica must be at or below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed. With each batch of samples and at the end of the analytical run, analyze a continuing calibration blank (CCB). The value of the CCB must be below the Report Limit (0.50 mg/L) for the run to continue. If the CCB is above the Report Limit, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Continuing verification of calibration: Analyze the initial calibration verification (ICV) sample after calibration. Analyze a continuing calibration verification standard (CCV) after every 10^{th} sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, the ICV or CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.5 Accuracy: At the start of an analytical run, analyze a laboratory fortified blank (LFB). The accuracy as percent recovery is calculated. If the recovery of the analyte falls outside the required control limits of 90-110%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analysis.

9.2.6 Matrix effects: Run a laboratory fortified matrix (LFM) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The same solution used to fortify the LFB is used to fortify the LFM. The accuracy, as percent recovery after background correction, is calculated. If the recovery of the LFM falls outside of 90-110% limits, the LFM is repeated. If the recovery of the repeat analysis also falls outside these control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the LFM of the diluted sample is within the control limits, then the recovery problem encountered with the LFM is considered to be matrix related, not system related, and the analysis may continue provided that the CCV is within acceptable limits. The diluted sample result is reported with an elevated report level reflective of the dilution used and the following remark code (DM) is added: "Report Level was changed due to matrix interference."

If the recovery of the LFM from the diluted sample falls outside the acceptable limits, the result is reported using an elevated report level reflective of the dilution used and the following comment is added: "Spike recovery was xx%."

9.2.7 Precision: Analyze a laboratory duplicate (LD) with each set of samples processed as a group, or 10% of the samples analyzed, whichever is greater. The absolute difference between duplicates and the relative percent difference (RPD) of the duplicates are calculated and used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.3 External verification of laboratory performance: Performance evaluation (PE) samples are analyzed as required for Federal certification. If the results are not within the control limits, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance (QA) Officer.

9.4 The MDL study is repeated annually, or when changes in analyst, instrumentation or instrument response occur. A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. For this SOP the lowest (0.50 mg/L) standard is used. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See 16.3) MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Dissolved Analysis: The filtration blank results must be below the report limit. If the filter blank is above the report limit, consult with a lead worker or supervisor to determine if the filter blank result should be subtracted from the sample results or if other action should be taken.

9.6 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of QCS, LFB, CCV, and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

9.7 A run is out of control when the external reference falls outside the acceptable limits. The run data is then rejected unless accepted by the Unit Supervisor.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 8 calibration standards and a calibration blank by diluting suitable volumes of calibration standard solution, as described in Section 7.7.

10.2 Process calibration standards and calibration blank as described in Section 11.

10.3 Read calibration standards and calibration blank in ascending concentration on the spectrophotometer.

10.4 Prepare calibration standard curve by plotting instrument response against concentration values. The curve used must be linear and not forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the spectrophotometer microprocessor. The calibration standard curve is accepted if the standard deviation (SD) of the difference between the standards and their true values are ≤ 0.3 and a correlation coefficient of 0.9990 is achieved. Also the concentrations of the standards must be within ± 10% of their true value except the 0.50 mg/L standard which can be ± 20% of its true value. Print out the calibration standard curve and the list of values for the standard curve. Write the SD on the calibration standard curve printout and print the curve showing the correlation coefficient.

10.5 After the calibration has been established, it must be verified by the analysis of a laboratory reagent blank (LRB), laboratory fortified blank (LFB) and a suitable quality control sample (QCS). The background level of the analyte in the ICB or LRB must be at or below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed. If measurements exceed ± 10% of the established LFB or QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis. A continuing calibration verification standard (CCV). A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) should be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 0.50. The results for the calibration verification standard (CCV) must be within ± 10% of the true value (0.10 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

S:\public\methods\sops.final-2000\General Chemistry SOPs (Final)\UV_VIS_IR.030.F05.doc

11.0 PROCEDURE

11.1 Turn spectrophotometer on to warm up (30 minutes).

11.2 If dissolved silica is requested, filter a filter blank and the sample through a 0.45 µm pore size syringe filter. Use the first portion of the filtrate to rinse the collection vessel.

11.3 Pipet 10 mL of each of the following standards into 50 mL polyethylene test tubes: 0.0 (calibration blank), 0.50, 1.0, 2.0, 5.0, 10.0, 15.0, 30.0, and 50.0 mg/L.

11.4 Pipet 10 mL of the 15.0 mg/L initial calibration verification (ICV) into a 50 mL polyethylene test tube.

11.5 Pipet 10 mL reagent water into a 50 mL polyethylene test tube for laboratory reagent blank (LRB).

11.6 Prepare a laboratory fortified blank (LFB) or laboratory fortified matrix spike (LFM) by adding 0.2 mL of 1000 ppm stock silica solution into a 50 mL polyethylene test tube. Add 10 mL reagent water or sample. The true value equals 20.0 mg/L.

11.7 Pipette 10 mL of each type of quality control sample into a 50 mL polyethylene test tube. Be sure to set up laboratory duplicates and laboratory fortified sample matrix's every 10 samples. The 0.10 mg/L continuing calibration verification (CCV) and the continuing calibration blank (CCB) should be set up every 10 samples and at the end of each run.

11.8 Place 10 mL of each sample, any filter blanks or an aliquot diluted to 10 mL, into corresponding 50 mL polyethylene test tubes. Set up laboratory duplicates and laboratory fortified sample matrixes every 10 samples.

11.8.1 For all samples that are not Bottle Blanks, set up a second test tube with 10 mL of sample. This will be the color blank. Do not shake the samples.

11.9 Add 0.2 mL of 1:1 HCl and 0.4 mL of ammonium molybdate to all standards and initial QC standards. NOTE: Develop calibration standards and blank before color developing samples.

11.10 Add ONLY 0.2 mL of 1:1 HCl to all color blanks. Omit the addition of ammonium molybdate since this causes the color development.

11.11 Mix all test tubes with the vortex and let stand for 5 to 10 minutes.

11.12 Add 0.4 mL oxalic acid to all tubes including the color blank tubes.

11.13 Mix all tubes with the vortex.

11.14 Allow color to develop for a minimum of 2 minutes but not more than 15 minutes from the addition of oxalic acid.

11.15 Set up spectrophotometer to read the color at 410 nm by recalling the stored program "Silicas". The color must be read after 2 minutes of development but before 15 minutes from the addition of oxalic acid.

11.15.1 See "Du Series 600 and 700 Spectrophotometer Basic Instrument Training Manual and Advanced Applications Training Manual" for operating instructions. Clean flow cell prior to run.

11.16 Read the calibration blank and standards on the spectrophotometer.

11.16.1 Make copy of standard curve.

11.16.2 Flush system with reagent water between each standard.

11.17 Color develop samples by repeating Sections 11.9 through 11.14.

11.18 Read samples on spectrophotometer. Remember the sample must color develop for a minimum of 2 minutes and must be read on the spectrophotometer before 15 minutes from the addition of oxalic acid.

11.18.1 Flush system with reagent water after every reading and at the end of the run.

11.18.2 Print results and label printout with analysis name and code, date of analysis, analysts' initials, and Standard Deviation of the curve.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calculations are performed by a microprocessor in the spectrophotometer (Beckman DU 600). The concentrations of the standards are in a template. The analyst reads the standards and the microprocessor uses the absorbances plotted against the actual concentration values to create a standard curve. When the absorbance of an unknown sample is read, the microprocessor uses an equation from the curve to determine the concentration.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file.

12.3 The minimum reporting level is 0.50 mg/L as SiO_2.

12.4 Results are reported in mg/L as SiO_2 to two significant figures.

12.5 Laboratory duplicates, LFB, LFM, and CCBs are highlighted. QCS, ICVs, CCVs are circled. The results are entered into the LIMS.

12.6 Subtract the concentration value for any color blanks from their respective sample result to correct for sample color or turbidity. Because the computer on the spectrophotometer computes the concentrations from the absorbencies, it is not possible to subtract the absorbance of the color blank from the absorbance of the sample.

12.7 The average concentration of any laboratory duplicate analysis is reported.

12.8 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 50.0 mg/L as SiO_2 are diluted and reanalyzed.

12.9 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1. Information pertinent to our laboratory's performance can be found in our Quality Assurance Manual, Section 9.

13.2. Current MDL data is available from the QA Officer.

13.3. Precision and accuracy data used for single laboratory testing will be summarized annually by the QA Officer.

14.0 POLLUTION PREVENTION

14.1. For information regarding the laboratory's pollution prevention policy and procedures see Public Health Laboratory Hazardous Waste Manual, DRAFT, October 1994.

14.2. The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3. For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1. The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reclamation, recycling, and purchasing.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Defined the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2. All waste from this method can be flushed down the drain.

15.3. For additional information regarding the laboratory's waste management policy, see Public Health Laboratory Hazardous Waste Manual, DRAFT, October 1994.

16.0 BIBLIOGRAPHY

16.1. Standard Methods for the Examination of Water and Wastewater, Method 4500- SiO_2 C, 20th Edition, 1998.

16.2. "Methods for Chemical Analysis of Water and Wastes." U.S. Environmental Protection Agency, Method 370.1, 1978.

16.3. "Appendix B to Part 136-Defination and Procedure for the Determination of Method Detection Limit- Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

16.4. "DU Series 600 and 7000 Spectrophotometer," Beckman Instruments, Inc., Manual SL7430-AA, March, 1995.

17.0 DIAGRAMS, FLOWCHARTS, VALIDATION DATA

17.1 The initial Demonstration of Capability data is on file; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

S:\public\methods\sops.final-2000\General Chemistry SOPs (Final)\UV_VIS_IR.030.F05.doc

Developed By: Elisabeth Dankert Date: 4/09/2001

Written By: Elisabeth Dankert Date: 4/09/2001

Revised By: Stephanie Peterson Date: 6/8/05
Stephanie Peterson, Env Analyst 1

Elisabeth Dankert Date: 6/1/05
Elisabeth Dankert, Env Analyst 3

Approved By: Keith Peacock Date: 6/8/05
Keith Peacock, BactiChem Unit Supervisor

Reviewed By: William Scruton Date: 6/8/05
William Scruton, QA Officer

Approved By: Louise S. Liao Date: 6-9-05
Louise Liao, Env Lab Section Manager

Approved By: Date: 6-14-05
Norman Crouch, PHL Division Director

PROCEDURE FOR THE DETERMINATION OF:

CHLORIDE AND SULFATE IN WATER BY ION CHROMATOGRAPHY

Table of Contents

1.0 SCOPE AND APPLICATION

1.1 Sulfates (SO42-) are widely distributed in the environment, occurring naturally and in man-made products. In water supplies, sulfate is usually combined with sodium or magnesium and may impart a bitter taste. Sulfate concentrations greater than 250 mg/L in drinking water may produce a laxative effect in people who are not acclimated to the sulfate level.

1.2 Chloride, in the form of the chloride (Cl-) ion, is one of the major inorganic anions in water and wastewater. The chloride concentration is higher in wastewater than in raw water because sodium chloride (NaCl) is a common component of the diet and passes unchanged through the digestive system. Along the sea coast, chloride may be present in high concentrations because of leakage of salt water into the sewage system. It also may be increased by industrial processes. High chloride content may harm metallic pipe and structures as well as growing plants.

1.3 This Standard Operating Procedure (SOP) covers the determination of the following inorganic anions:

Chloride Sulfate

1.4 This SOP is applicable to the measurement of chloride and sulfate in finished drinking water, surface water, and ground water.

1.5 This SOP can be used for sample analysis under the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA).

1.6 The laboratory is certified by the US EPA to use the SOP for sample analysis under the SDWA.

1.7 The working range for each anion is as follows:

Analyte	Range, (mg/L)
Chloride	1 to 1000
Sulfate	1 to 400

1.8 These ranges are based on a 10 µL sample loop. Dilutions are prepared for concentrations greater than the upper limit of the range defined above.

1.9 All samples are filtered through a 0.20 µm membrane filter as part of the analysis to protect the instrumentation.

1.10 This SOP is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram.

1.11 Users of the SOP data should state the data-quality objectives prior to analysis. Users of the SOP must demonstrate the ability to generate acceptable results with this SOP, using the procedures described in Section 9.

1.12 This SOP is compliant with the requirements of, except as noted:

EPA 300.1 (A)

1.12.1 The calibrated range for this SOP is more than 2 orders of magnitude. This differs from the recommended two orders of magnitude in EPA method 300.1. The range is accepted because it meets all the parameters defined in Section 9 of this SOP.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample is injected into an ion chromatograph. The chloride and sulfate anions are separated through the use of a guard column and separator column and then measured through the use of a suppressor and conductivity detector.

2.2 An extraction procedure must be performed to use this method for solids.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Method Blank (MB) immediately

before any samples are analyzed and periodically throughout the run as needed.

4.2 Chromatographic interferences can be divided into three categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependent coelution, where the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion, or where the higher than typical concentrations of the target analyte cause the window of the retention time to be larger than what is calibrated for and it is picked up as a non-detect in the integration; and ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.2.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, changing the detection systems, or selective removal of the interference with pretreatment. The analyst must verify that these changes do not adversely affect performance by repeating and passing all the QC criteria in Section 9.

4.2.2 Sample dilution may resolve interferences due to concentration dependent coelution or ionic character displacement. Sample dilution will alter the Minimum Reporting Limit (MRL) by the amount of the dilution.

4.2.3 Pretreatment of the sample can be an effective means to eliminate certain matrix interferences. If used, all instrument calibration standards and QC samples should be pretreated in the same manner as pretreated field samples.

4.3 All samples and standards are filtered through a 0.20 µm filter before analysis to prevent damage to instrument columns and flow systems.

4.4 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis. It is the responsibility of the analyst to confirm

that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

4.5 Other compatible procedures for the removal or suppression of interferences may be employed provided they do not adversely affect the overall performance of the method.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02.1	Occupational Safety and Health
420.01.1	Right-to-Know

5.3 In addition, the analyst should read the MDH Public Health Laboratory Division – Chemical Hygiene Plan (http://fyi.health.state.mn.us/phl/safety/index.html). Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Health and Safety Officer.

5.4 The analyst should read the Lab Building Emergency Procedures plan (http://fyi.health.state.mn.us/phl/safety/index.html) and know what to do in a variety of emergency situations.

5.5 Protective eyewear should be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.6 The analyst may contact the Employee Hazard Hotline regarding employee exposures to hazardous chemicals (1-888-673-7466 Toll Free). The system is available 24 hours per day, seven days per week.

5.7 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.7.1 Dichloroacetic acid, potassium salt

5.7.2 Potassium Hydroxide (Eluent Generator Cartridge)

5.7.3 Hydrochloric Acid

5.7.4 Sodium Chloride

5.7.5 Potassium Sulfate

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance – Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Weigh boats, plastic, disposable.

6.3 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A.

6.4 Fixed and adjustable pipettes.

6.5 Ion Chromatograph: Dionex ICS 3000 or equivalent. An analytical system complete with all required accessories, tubing and pumps to operate the system, including, but not limited to, the items listed below:

6.5.1 Autosampler: Dionex AS40 or equivalent.

6.5.2 Sample Vials: Dionex 5 mL Vials with filter caps, 250 each (P/N 038141) or equivalent.

6.5.3 Injection Valve: Dionex High-pressure 6-port Injection valve (P/N 061961) or equivalent.

6.5.4 Sample Loop: Dionex 10 µL sample loop (P/N 042949) or equivalent.

6.5.5 Dionex CR-ATC (Anion Continuously Regenerated Trap Column) (P/N 060477) or equivalent.

6.5.6 Anion Suppressor Device: Dionex Anion Self Regenerating Suppressor (ASRS) 300 4mm (P/N 064554) or equivalent.

6.5.7 Detector: Dionex Conductivity Detector (P/N 061830) or equivalent.

6.5.8 Chromeleon Software (version 6.8).

6.5.9 Anion Guard Column: Dionex IonPac AG18 (P/N 060551), 4 mm x 50 mm column, or equivalent.

6.5.10 Anion Separator Column: Dionex IonPac AS18 (P/N 060549), 4 mm x 250 column, or equivalent.

6.5.11 Dionex Eluent Reservoir 2 L Bottle (P/N 044129) or equivalent. Four bottles are used in parallel to optimize the system.

6.5.12 Dionex Eluent Degasser (P/N 062137) to degas eluent in-line or equivalent.

6.5.13 Compressed Gas: Helium, to degas reagent water to make eluent, and to maintain pressure in eluent reservoir tanks.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 megohm-cm at 25°C and free of the analytes chloride and sulfate.

7.2 Only Analytical Reagent (AR) grade or American Chemical Society (ACS) grade chemicals should be used.

7.3 Eluent: Dionex RFIC Eluent Generator Cartridge III Potassium Hydroxide (P/N 074532) or equivalent.

7.4 1 M HCl: In a 1-L volumetric flask, dilute 83 mL hydrochloric acid in about 700 mL of reagent water. Dilute to the mark with reagent water, and invert to mix. Prepare in a fume hood. This is used to clean the column; refer to Dionex Reference Library for instructions.

7.5 Surrogate Solution: 1000 mg/L Dichloroacetate (DCA) Solution: In a 500 mL volumetric flask, dissolve 0.65 g dichloroacetic acid, potassium salt

(Cl_2CHCO_2K, CASRN 19559-59-2) in reagent water. Dilute to mark and invert to mix. This solution is stable for 3 months unless signs of degradation appear.

7.6 Calibration Standards:

7.6.1 10000 mg/L Chloride Stock Standard (Cl^-): In a 1 L volumetric flask, dissolve 16.485 g sodium chloride (NaCl, CASRN 7647-14-5) that has been dried at 105 °C for 30 minutes, in reagent water. Dilute to the mark with reagent water and invert to mix. Solution is stable for 6 months when stored at 4 °C.

7.6.2 1000 mg/L Chloride Stock Standard (Cl^-): In a 100 mL volumetric flask, add 10 mL of 10000 mg/L Chloride Stock Standards in reagent water. Dilute to the mark with reagent water and invert to mix. Solution is stable for 6 months when stored at 4 °C.

7.6.3 5000 mg/L Sulfate Stock Standard (SO_4^{2-}): In a 1 L volumetric flask, dissolve 9.07 g of potassium sulfate (K_2SO_4, CASRN 7778-80-5) that has been dried at 105 °C for 30 minutes, in reagent water. Dilute to the mark with reagent water and invert to mix. Solution is stable for 6 months when stored at 4 °C.

7.6.4 1000 mg/L Sulfate Stock Standard (SO_4^{2-}): In a 100 mL volumetric flask, add 20 mL of 5000 mg/L Sulfate Stock Standard in reagent water. Dilute to the mark with reagent water and invert to mix. Solution is stable for 6 months when stored at 4 °C.

7.6.5 Working Calibration Standards: Prepare standards as follows:

Std Name	Final Vol. with ASTM Type II (mL)	Chloride Working Std Conc. (mg/L)	Vol. 1000 mg/L Cl Stock (mL)	Vol. 10000 mg/L Cl Stock (mL)	Sulfate Working Std Conc. (mg/L)	Vol. 1000 mg/L SO_4 Stock (mL)	Vol. 5000 mg/L SO_4 Stock (mL)	DCA Working Std Conc. (mg/L)	Vol. 1000 mg/L DCA Stock (mL)
CAL1/RLV (G)	250	1	0.25		1	0.25			
CAL2 (F)	250	10	2.50		10	2.50			
CAL3 (E)	250	100		2.50	20	5.00			
CAL4 (D)	250	250		6.25	50		2.50	8.0	2.00
CAL5/CCV (C)	500	500		25.00	100		10.00	10.0	5.00
CAL6 (B)	200	750		15.00	200		8.00	13.0	2.60
CAL7 (A)	200	1000		20.00	400		16.00	15.0	3.00
BS/MS	50	6666.6		33.33	1666.6		16.67		

Prepare Monthly.

7.7 The Quality Control Standard (QCS) or Secondary Verification Standard (SCV) is purchased and prepared according to instructions provided by the manufacturer.

7.8 Blank Spike and Matrix Spike: In a 5 mL vial, add 300 µL prepared BS/MS Spiking Solution to 4.7 mL reagent water or sample. Add 50 µL of 1000 mg/L DCA Solution to the sample.

7.9 All reagents should be discarded if precipitate or growth appears.

7.10 All reagents and standard are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are collected in 125-mL, 250-mL, 1-L, 2-L plastic bottles and stored at 4°C prior to analysis.

8.2 No preservatives should be added to the samples. The chloride and sulfate analyses cannot be performed on an acidified sample.

8.3 Samples are analyzed within 28 days of collection date.

8.4 Maximum holding time is 28 days when stored at 4°C ± 2°C.

8.5 All samples must be filtered by using a 0.45 micron nylon filter to prevent damage to the valves and columns. This is accomplished with the use of the autosampler and using vials with a fitted filter.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability (IDC): The analyst must be able to demonstrate that they can generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial Calibration: The linear calibration range (LCR) must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument.

9.1.2 External Verification of Calibration: A second-source calibration verification (SCV) from an external source is analyzed. The results of the SCV must be within ± 15 % of the established SCV value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limit (MDL) Study: A minimum of 7 replicate laboratory Control Samples (BS) are spiked at a value 1 to 5 times the estimated detection limit and processed over a period of three days. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated. Once the IDC has been established for this SOP, the Unit

Supervisor may waive this requirement for individual analysts if the reference method does not specifically require an MDL study for new analysts.

9.1.4 Initial Precision and Accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.1.6 Demonstration of Low Background: Analyze at least one Method Blank (BLK) to determine reagent or laboratory contamination. The BLK result must meet the criteria established for the on-going demonstration of low background in Section 9.2.3.

9.1.7 Other Requirements for an IDC: An IDC needs to be repeated if there are significant changes to the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis, or when a change in analyst occurs. Consult with the Quality Assurance Officer (QAO) to determine if any changes require an IDC.

9.1.8 IDC Documentation: An IDC for each analyst must be on file in the QA office along with an IDC for the method, matrix, and instrument.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

Note: DCA must be added to all QC and field samples at a concentration of 10 mg/L.

9.2.1 Calibration: Calibrate the instrument whenever the curve verification fails, or monthly with new standards, with a calibration blank and at least 3 calibration standards covering the range of sample results and within the linear calibration range (LCR) of the analyte. Prepare the

calibration standard curve by plotting instrument response against concentration values. A calibration curve will be fitted to the calibration standard concentration/response data using the instrument's computer. The calibration standard curve is accepted if a correlation coefficient of 0.9950 or better is achieved.

9.2.2 Instrument Performance Check Solution (ICV): The Initial Calibrations Verification Standard is to be evaluated as the instrument performance check solution in order to confirm proper instrument performance. Recovery of the ICV must be 85-115%. If an analyte is outside the interval, CCV is reanalyzed. If the analyte is still outside the ± 15% limit, the instrument is recalibrated.

9.2.3 Chromatographic Performance Check: Use the initial calibration verification standard (ICV) to confirm proper instrument performance. With each run, calculate the Peak Gaussian Factor (PGF) to verify proper chromatographic performance, which measures peak symmetry. In addition, monitor the retention time drift in the surrogate peak over time.

9.2.3.1 Use the surrogate peak (DCA) on the ICV to determine the PGF, as follows:

9.2.3.2 $$PGF = \frac{1.83 \times W\frac{1}{2}}{W\frac{1}{10}}$$

Where: $W\frac{1}{2}$ is the peak width at half height

$W\frac{1}{10}$ is the peak width at tenth height

9.2.3.3 The PGF must fall between 0.08 and 1.15 in order to demonstrate proper instrument performance.

9.2.4 Monitor the retention time of the surrogate in the ICV each run. The retention time for the surrogate in the ICV must be closely monitored

on each day of analysis and throughout the lifetime of the analytical column. Small variations in the retention time can be anticipated when a new solution of eluent is prepared, but if shifts of more than 2% are observed in the surrogate retention time some type of instrument problem is present. Potential problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The chromatographic profile (elution order) of the target anions following an ion chromatographic analysis should closely replicate the profile displayed in the test chromatogram that was shipped when the column was purchased. As a column ages, it is normal to see a gradual shift and shortening of retention times. If any of the retention times have noticeable shift, by less than 80% of the original recorded value, the column may require cleaning or replacement. This is particularly true if resolution problems are beginning to become common between previously resolved peaks. Record the retention times for the surrogate and all the target anions to provide evidence of an analytical column's vitality, in the instrument manual.

9.2.5 External Verification of Calibration: Analyze a second- source calibration verification standard (SCV), from an external source immediately after calibration to verify instrument performance. The results of the SCV must be within ± 15% of the target value; otherwise corrective action is taken before analyzing samples.

9.2.6 Demonstration of Low Background: At the beginning each batch, analyze a blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK or ICB must be below the report level; otherwise the source of the contamination is investigated and corrected before samples are analyzed. Analyze a continuing calibration blank (CCB) every 10 samples and at the end of the run. The CCB must be less than the report level (MRL). If the CCB is above the Report Level, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.7 Report Level Verification (RLV) Check: A Report Level Verification (CRL) check must be performed each time the instrument is calibrated. The CRL check is performed by analyzing a calibration standard at or below the report level. (The CRL check sample is not required to be processed through the entire SOP.) The percent recovery of the CRL must be within ± 40%.

9.2.7.1 If the percent recovery of the CRL standard is outside the acceptance criteria, the analyst must either: 1) repeat the verification check or 2) recalibrate and then perform the CRL check. If the repeat CRL is within acceptance criteria, or if the instrument recalibration results in a CRL check that is within acceptance criteria, the analyst may proceed with the analytical run. If the second verification check is not within acceptance criteria, the analyst must either: 1) recalibrate the instrument and then perform the CRL check once again, or 2) perform the CRL at a higher concentration level.

9.2.7.2 If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the report level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed CRL check using the elevated report level until a new calibration curve and CRL standard meet the acceptance criteria.

9.2.8 Continuing Verification of Calibration: Analyze a continuing calibration verification standard (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 15% of its expected value. If an analyte is outside the interval, CCV is reanalyzed. If the analyte is still outside the ± 15% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.9 Accuracy: With every batch of 20 samples processed as a group, analyze a laboratory control sample (BS). The BS should be prepared

at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the MS. Accuracy (as percent recovery) is calculated as follows:

$$\%\ \text{Recovery} = \frac{\text{Found Concentration of BS}}{\text{True Concentration of BS}} \times 100$$

If the recovery of the analyte falls outside the required control limits of 85-115%, the analyte is judged out of control. The source of the problem should be identified and the situation resolved before sample analysis can continue.

9.2.10 Matrix Effect: Run a laboratory matrix spike (MS) with each batch of 20 samples processed as a group, or a minimum of 10% of the field samples analyzed, which ever is greater. The same solution used to fortify the blank spike (BS) is used to fortify the MS. Accuracy (as percent recovery after background correction) is calculated as follows:

$$\%\ \text{Recovery} = \frac{\text{Found Concentration of MS - Concentration of Matrix Sample}}{\text{True Concentration of MS}} \times 100$$

If the recovery of the MS falls outside of 85-115% limits, the MS is repeated. If the recovery of the repeat analysis also falls outside the control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the analyte still falls outside the designated MS recovery range and the BS, and ICV/CCV for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be matrix induced and the results for the diluted sample and the MS are reported using an elevated report level reflective of the dilution used and the qualifier QD: "Recovery in MS not within acceptance limits" is added to the MS.

9.2.10.1 If the MS recovery of the diluted sample is within acceptable limits, the sample is reported with an elevated Report Level reflective of the dilution used.

9.2.11 Surrogate Recovery: Calculate the surrogate recovery from all analyses using the following formula:

$$\text{Percent Recovery} = \frac{\text{Surrogate Recovered Concentration}}{\text{Surrogate Fortified Concentration}} \times 100$$

Surrogate recoveries must fall between 90-115% for proper instrument performance and analyst technique to be verified. If the surrogate recovery falls outside the 90-115% recovery window, analysis error is evident and sample reanalysis is required. Poor recoveries could be the result of imprecise sample injection, analyst fortification errors, or complicated samples.

9.2.12 Precision: Analyze a laboratory duplicate (DUP) with each batch of field samples processed as a group, or10% of the field samples analyzed, whichever is greater.. Calculations of the absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.12.1 Calculate the relative percent difference of the duplicates using the following formula:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = concentration of sample

D = concentration of duplicate sample

9.2.12.2 Duplicate acceptance criteria:

Concentration Range	Criteria:
RL to 10xRL	None
10xRL to highest calibration std	RPD ≤ 10%

9.2.12.3 If the duplicate concentration is between the RL and 10xRL, and the RPD is greater than 10%, the qualifier QH is added to the duplicate: "RPD between sample duplicates not within acceptance limits. Analyte concentration in the samples too low for proper evaluation."

9.2.12.4 If the duplicate fails to meet the above criteria, the samples should be reanalyzed to verify poor duplicate analysis RPD. If the repeated duplicate is still not within acceptable limits, the samples must be reported with a qualifier identifying the sample analysis result as yielding poor duplicate analysis RPD.

9.3 External verification of laboratory performance: Proficiency test (PT) samples are analyzed as required for Federal certification. If the results are not within acceptance criteria, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance Officer.

9.4 The MDL study is repeated when changes in analyst, instrumentation or instrument response occur. A minimum of 7 replicate laboratory fortified blanks (LFB) are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3)

MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of SCV, CRL, CCV and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 7 calibration standards by diluting suitable volumes of calibration standard solution, as described in Section 7.5.

10.2 Process calibration standards and calibrate the instrument as described in Section 11. Refer to the Dionex Reference Library for more details.

10.3 Prepare calibration standard curve by plotting instrument response against concentration value. The curve should be calculated using the peak area and not forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the Dionex Chromeleon Chromatography Management System. A second-order fit is acceptable, provided all QC performance criteria are acceptable (Section 9.3) A curve is accepted if the correlation coefficient is 0.9950 or greater. If the results are still outside these criteria, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated.

10.4 After the calibration has been established, it must be verified by the analysis of an ICV, ICB, CRL, and SCV.

10.4.1 The background level of the analyte in the ICB or CCB must be at or below the RL; otherwise the source of the contamination is investigated and corrected before samples are analyzed.

10.4.2 The results of the CRL must be within ± 40% of the true value in order to proceed. If it is not, follow the procedure outlined in Section 9.2.4.

10.4.3 If measurements exceed ± 15% of the established QCS value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.4.4 Transfer the calibration statistics into Element when calibration is complete.

10.4.5 A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) must be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 1.0 mg/L for both sulfate and chloride. The results for the calibration verification standard (CCV) must be within ± 15% of the true value (500 mg/L chloride and 100 mg/L sulfate). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

10.4.6 The BLK and BS within each analytical batch must meet the requirements below in order for that batch to be reported. All samples within the batch must be repeated is the BLK and BS are outside the acceptance limits.

Parameter	Acceptance Criteria
BLK	Less than RL
BS	85-115%

11.0 PROCEDURE

11.1 System Start-up

11.1.1 The ICS-3000 works best when water and eluent are continually flowing through the system, even when not analyzing samples.

11.1.2 Use Dionex IonPac AS18 analytical column in line with the IonPac AG18 guard column. If putting the column on after it has been sitting, or if the eluent has not been flowing, let the eluent flow for at least 1 hour to equilibrate the column before analyzing samples. Check connections to ensure there are no leaks.

11.1.3 Fill eluent reservoir bottles with degassed reagent water. Degas reagent water with He at 140 kPa (20 lb/in^2) through a helium degassing tube (Lachat part number 50100). Bubble He vigorously

through the solution for at least 10 minutes. Reservoir bottles are kept under pressure from the helium tank to decrease the carbonate peaks.

11.1.4 Prime the pump to eliminate air bubbles in the lines. Turn the priming knob on the pump a quarter turn and turn on prime in the Chromeleon software instrument panel. Close the knob before resuming normal flow after priming is done.

11.1.5 Use data system parameters below for the instrument panel to set-up for the analytical run:

Parameters	**Instrument Conditions**
Eluent	25 mM KOH
Current	100 mA
Eluent Flow Rate	1.2 mL/min
Sample Loop	10 µL
Expected pressure	2000-3000 psi
Analytical Column	IonPac® AS18
Guard Column	IonPac® AG18
Analysis time	~ 30 minutes

11.1.5.1 Turn on flow to 1.2 mL/min. Turn on eluent generator and set concentration to 25 mM. Turn on CR-ATC.

11.1.5.2 Turn on suppressor. Set current to 100 mA. Background signal for the conductivity detector should be 2 µS or less.

11.1.5.3 Background pressure should be between 2000 – 3000 psi.

11.2 Sample Preparation:

11.2.1 Follow the sample collection, pretreatment, and preservation procedures given in Section 8.

11.2.2 Prepare all samples with the DCA surrogate solution. Add 50 µL of 1000 mg/L DCA solution (Section 7.5) to a 5 mL vial, add 5 mL of sample. Add a filter with the Dionex tool to push down the filter

evenly into the vial. Sample is now ready for analysis. The true value of the DCA concentration in every sample is 10 mg/L.

11.2.3 Add 50 µL of 1000 mg/L DCA solution to a 5 mL aliquot of all samples, batch QC samples, and the SCV. The CRL, CCV and CCB have DCA in the solution already and don't need to be spiked.

11.2.4 Prepare a blank spike (BS) by adding 4.7 mL reagent water to a vial. Add 300 µL of prepared BS/MS Spiking Solution and 50 µL of 1000 mg/L DCA solution to the vial and cap with filter. Invert to mix. Run one BS with each batch of no more than 20 samples. The true value is 400 mg/L for chloride and 100 mg/L for sulfate.

11.2.5 Prepare a matrix spike (MS) by adding 4.7 mL sample to a vial. Add 300 µL of prepared BS/MS Spiking Solution and 50 µL of 1000 mg/L DCA solution to the vial and cap with filter. Invert to mix. Run two MS with each batch of no more than 20 samples. The true value is 400 mg/L for chloride and 100 mg/L for sulfate.

11.2.6 Pour off the calibration standards in ascending order into vials and cap with filter. Pour off enough CCV and CCB standards to be run every 10 samples and at the end of the run. The true value of the CCV is 500 mg/L chloride and 100 mg/L sulfate. The CCB should be under the RL of 1.0 mg/L for both analytes.

11.3 Create a sequence in Element Database and export the file into the Chromeleon Chromatography Management System. The Chromeleon system is an automated constant volume injection system that will tabulate peak response against concentration.

11.4 Load standard vials and sample vials in the order of the sequence into the AS40 autosampler and toggle to Run from Hold.

11.5 The autosampler should have the following parameters selected for running:

11.5.1 Vial Type: 5 mL and Sample Rinse.

11.5.2 Set-up: Inj Type = Loop, Inj Mode = Prop, Bleed = Off, Inj/Vial = 1

11.5.3 Sampler: Injection and First

11.5.4 Operation: Lcl (Local, not Remote) and Run (toggle from Hold)

11.6 To start the analytical run, press the start batch icon in Chromeleon and complete the wizard. After acceptable curve is achieved and initial QC is obtained and acceptable, continue with analysis

11.7 In order to perform USEPA compliance monitoring, the suppressor must be in-line during sample processing. Any data generated without the in-line, fully activated suppressor cartridge, cannot be reported for compliance monitoring.

11.8 If one or more analyte responses exceed the calibration range, dilute the sample with reagent water, add 50 µL of 1000 mg/L DCA solution and reanalyze.

11.9 Should more complete resolution be needed between peaks, the eluent can be diluted 10% to 30%. This will increase separation but will also cause the later eluting analytes to be retained longer. This dilution should not be considered a deviation from the method. Alternately, slowing the eluent flow rate by 20 % to 40% can increase separation slightly. The analyst must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9.

11.9.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely affect the MDLs for each analyte.

11.10 System and Procedure Notes

11.10.1 For information on system maintenance and troubleshooting refer to the Dionex Reference Library.

11.10.2 Do not suddenly release the pressure from the columns or they may be damaged. Turn off flow and wait for the pressure to subside to less than 100 psi before disconnecting anything from the system.

11.10.3 The retention times for each of the analytes are affected by eluent concentration, flow rate, extreme range of analytes concentration, and column performance. The user may need to make minor adjustments to the retention times to ensure each peak is identified correctly and integrated properly.

11.10.4 As preventative maintenance, the guard column should be replaced periodically. The guard column can be replaced more frequently than the analytical column.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The Chromeleon Chromatography Management System will prepare a calibration curve for each analytes by plotting instrument response, as peak area, against standard concentration. Sample concentration is calculated by comparing sample response versus standard concentration. If a sample has been diluted, multiply the response by the appropriate dilution factor.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file in the QA Office.

12.3 The Initial Demonstration of Capability data are on file in the QA Office; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

12.4 The minimum report levels are listed below:

Analyte	Report Limit
Chloride	1 mg/L
Sulfate	1 mg/L

12.5 Results are reported in mg/L to three significant figures.

12.6 Sample results and quality control data are transferred electronically to the Element Database by the analyst.

12.7 The concentration of the original sample is reported and the laboratory duplicate analysis is reported as the duplicate value.

12.8 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 1000 mg/L Cl^- and/or 400 mg/L SO_4^{-2} are diluted and reanalyzed. If the value is below the report level, then the dilution was too great and should be reported using a greater sample volume portion.

12.9 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1 Information pertinent to our laboratory's performance is available in the QA Office.

13.2 Current MDL data are available in the QA Office.

13.3 Precision and accuracy data are available in the QA Office.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult, "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C., 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reduction, reclamation, recycling.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.

- Prevent pollution at the source whenever possible.
- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 All waste from this method can be flushed down the drain.

15.3 For additional information regarding the laboratory's waste management policy, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

16.0 BIBLIOGRAPHY

16.1 Pfadd, J.D., Hautman, D.P. and Munch, D.J., USEPA Method 300.1, "Determination of Inorganic Anions by Ion Chromatography," NERL, Office of Research and Development, USEPA, Cincinnati, OH 45368, rev. 1.0, 1997.

16.2 "Appendix B to Part 136-Definition and Procedure for the Determination of Method Detection Limit-Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

16.3 "Dionex Reference Library," Dionex Corporation, November 2010. (CD-ROM)

Approved By: /s/ Jeffrey Brenner Date: 11-15-2011
Jeffrey Brenner, Inorganic Unit Supervisor

Approved By: /s/ Paul Moyer Date: 11-15-2011
Paul Moyer, Environmental Lab Section Manager

REVISION NUMBER	AUTHOR/ REVISOR	REVISION DATE	DESCRIPTION OF CHANGE
0	Dane Huber	03-23-13	This is the first release for a controlled, standardized format for General Chemistry.

PROCEDURE FOR THE DETERMINATION OF:

DISSOLVED SULFIDE IN WATER AND SOIL WITH INLINE DISTILLATION
BY
FLOW INJECTION ANALYSIS COLORIMETRY

Sulfide & Acid Volatile Sulfide

Table of Contents

Section **Page**

SCOPE AND APPLICATION

1.1 Sulfide is often present in groundwater, especially in hot springs. Its common presence in wastewaters comes from the decomposition of organic matter, industrial wastes, mine run off, and the bacterial reduction of sulfate. Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor-nuisances. The threshold odor concentration of H_2S in clean water is between 0.025 and 0.25 ug/L. Gaseous H_2S is very toxic and has claimed the lives of numerous sewer workers. At levels toxic to humans it interferes with the olfactory system so that it cannot be detected. It attacks metals directly and indirectly has caused serious corrosion of concrete sewers because it is oxidized biological to H_2SO_4 on the pipe wall. Dissolved H_2S is toxic to fish and other aquatic organisms.

1.2 Hydrogen sulfide, in sediments, can combine with iron and other metals to form slightly-soluble precipitates. Acid-volatile sulfides (AVS) is an main class of metal sulfides and is considered to be the key binding phase for controlling bioavailability of toxic metals in anoxic sediments.

1.3 This Standard Operating Procedure (SOP) is applicable to the measurement of sulfide in drinking, ground, and surface waters, and domestic and industrial wastes.

1.4 This SOP can be used for sample analysis under the Clean Water Act (CWA).

1.5 The working range is 0.01 to 2.0 mg/L. Dilutions are prepared for concentrations greater than 2.0 mg/L. The working range of the reference method is 0.01 to 2.0 mg/L.

1.6 This SOP is compliant with the requirements of SM4500-S2 E using the Lachat QuikChem® Method 10-116-29-3-A. Approval letters (Appendices I and II).

2.0 SUMMARY OF METHOD

2.1 The method is based on the methylene blue reaction.

2.2 Hydrogen sulfide (H_2S) is released by means of in-line distillation under acidic conditions. The gaseous H_2S is separated by a diffusion cell, and then absorbed by a sodium hydroxide solution. The method does not recover sulfide from insoluble matter such as CuS or suspended solids.

2.3 The distilled hydrogen sulfide (H_2S) then reacts in acid media and in the presence of ferric chloride with two molecules of N,N-dimethyl-p-phenylenediamine to form methylene blue. The resulting color is read at 660 nm and is proportional to the concentration of H_2S in the sample.

3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the laboratory appear in the QA Manual.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Method Blank (BLK) with each batch of no more than 20 samples.

4.2 Strong reducing agents at levels of several hundred ppm inhibit color formation.

4.3 Iodide interferes at levels greater than 2 mg/L.

4.4 The method is relatively free from interferences because gas dialysis separates the sulfide from sample matrix.

4.5 During sample collection, sulfide might be lost by oxidation reaction with air or oxidizing agents in sample, such as chlorine.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

POLICY #	TITLE
902.02.1	Occupational Safety and Health
420.01.1	Right-to-Know

5.3 In addition, the analyst should read the MDH Public Health Laboratory Division – Chemical Hygiene Plan (http://fyi.health.state.mn.us/phl/safety/index.html). Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Health and Safety Officer.

5.4 The analyst should read the Lab Building Emergency Procedures plan (http://fyi.health.state.mn.us/phl/safety/index.html) and know what to do in a variety of emergency situations.

5.5 Safety glasses should be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.6 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.7 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.7.1 Hydrochloric Acid

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance – Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A. All non-disposable glassware must be rinsed with 1:1 Hydrochloric acid (HCl) followed by three rinses with reagent water prior to use.

6.3 Fixed and adjustable pipettes.

6.4 Flow injection analysis equipment designed to deliver and mix samples and reagents in the required order and ratios (Lachat Instrument or equivalent).

6.4.1 Autosampler

6.4.2 Multichannel proportioning pump

6.4.3 Reaction unit or manifold

6.4.4 Colorimetric detector

6.4.4.1 Flow Cell: 10 nm, 80 µL.

6.4.4.2 Interference Filter: 660 nm

6.4.5 Omnion® software (version 3.0)

6.4.6 Printer

6.4.7 Lachat Special Apparatus

6.4.7.1 Heating Unit

6.4.7.2 PVC pump tubing must be used for this SOP

6.5 Disposable 13X100 mm test tubes (use once and discard)

6.6 Disposable 5ml safety lock syringe and needles (use once and discard)

6.7 Vortex mixer

6.8 Acid-Volatile

6.8.1 60 mL Teflon vials

6.8.2 33 mL Teflon transfer caps

6.8.3 0.125" OD x .062" Teflon tubing

6.8.4 Flow meters

6.8.5 Multi-position Stir Plate

6.8.6 High purity nitrogen

6.8.7 50 mL plastic digestion tubes and caps

6.8.8 Drying oven equipped with digital thermometer, for operation at 95° C and 180° C

6.8.9 Desiccating cabinet

6.8.10 Moisture indicating desiccant: Drierite: 97% $CaSO_4$ CAS# 778-18-9 and 3% $CoCl_2$ CAS#7646-79-9

6.8.11 Heat resistant trays

6.8.12 57 mm Aluminum weighing dishes or equivalent

6.8.13 Forceps

6.8.14 Stir plate

6.8.15 Balance data transfer software (i.e. Collect 6.1)

6.8.16 Excel spreadsheet template with proper calculations.

7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 mega ohm-cm at 25°C and free of the analyte sulfide.

7.2 Only Analytical Reagent (AR) grade or American Chemical Society (ACS) grade chemicals should be used.

7.3 Standardized 0.0250 N Iodine Solution: Purchased commercially.

7.4 Standardized 0.0250 N Sodium Thiosulfate Titrant: Purchased commercially.

7.5 Starch Indicator Solution 2% w/v: Purchased commercially.

7.6 Degassing with Helium: To help prevent bubble formation, reagent water used to make reagents should be degassed. Use 20 lb/in^2 through a helium degassing wand. Bubble He through the reagent water for at least 10 minutes.

7.7 Hydrochloric Acid, 3 M: In an acid-rinsed, 1-L volumetric flask, add 600 mL of degassed reagent water, then slowly add 248 mL of concentrated hydrochloric acid (HCl). Dilute to 1-L with degassed reagent water. Prepare fresh monthly.

7.8 Hydrochloric Acid, 0.20 M: In an acid-rinsed, 1-L volumetric flask, add 700 mL of degassed reagent water, then add 16.5 mL of concentrated hydrochloric acid (HCl). Dilute to 1-L with degassed reagent water.

7.9 Sodium Hydroxide, 0.025 M: In an acid rinsed, 2-L volumetric flask, add 2 g of sodium hydroxide (NaOH) to approximately 800 ml of degassed reagent water. Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh daily. This reagent is used for standards diluent and carrier reagent. Remake 2-L portions as needed.

7.10 N,N-Dimethyl-p-phenylenediamine Reagent: In an acid-rinsed, 1-L volumetric flask, dissolve 1.0 g N,N-Dimethyl-p-phenylenediamine

[$(CH_3)_2NC_6H_4NH_2 \cdot 2HCl$] in approximately 800 mL 3 M hydrochloric acid reagent. Stir until dissolved. Dilute to volume with 3 M hydrochloric acid reagent. Prepare fresh monthly. Degas if necessary.

7.11 Ferric Chloride Reagent: In an acid-rinsed, 500-mL volumetric flask, dissolve 6.65 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in approximately 450 mL 0.20 M hydrochloric acid reagent. Stir until dissolved. Dilute to volume with 0.20 M hydrochloric acid reagent. Prepare fresh monthly. Degas if necessary.

7.12 Digestion Solution: In an acid-rinsed, 1-L volumetric flask, add approximately 700 mL of degassed reagent water, then add 90 mL of concentrated phosphoric acid (H_3PO_4). Dilute to volume with degassed reagent water. Prepare fresh monthly. Degas if necessary.

7.13 Alkaline Antioxidant Reagent: In an acid rinsed, 500-mL volumetric flask, add approximately 300 mL of degassed reagent water, then add 40 g sodium hydroxide (NaOH), 17.5 g ascorbic, and 33.5 g disodium ethylenediamine tetraacetate dehydrate ($Na_2EDTA \cdot 2H_2O$). Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh monthly. Degas if necessary.

7.14 Zinc Acetate Preservative, 2N: In an acid rinsed, 200-mL flask, add approximately 100 mL degasses reagent water, then add 88 g zinc acetate dehydrate ($(Zn(O_2CCH_3)_2 (H2O)_2$). Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh every 6 months.

7.15 NaOH preservative, 15 M: In an acid rinsed, 200-mL flask, add approximately 100 mL degassed reagent water, then add 125 g sodium hydroxide pellets (NaOH). Stir until dissolved. Dilute to volume with degassed reagent water.

7.16 Acid –Volatile Reagents

7.16.1 NaOH, 2N: In an acid rinsed, 500-mL flask, add approximately 300 mL degassed reagent water, then add 100 mL 10N NaOH. Dilute to volume with degassed reagent water. Prepare freshly each month.

7.16.2 Acid-volatile Catch Solution: In an acid rinsed, 500 mL flask, add approximately 300 mL degassed reagent water, then add 100 mL alkaline antioxidant reagent and 12.5 mL 2N NaOH. Dilute to volume with degassed reagent water. Prepare freshly daily.

7.16.3 Hydrochloric Acid, 9N: In an acid rinsed, 250 mL flask, add approximately 100 mL degassed reagent water, then slowly add 186 mL concentrated hydrochloric acid. Dilute to volume with degassed reagent water.

7.16.4 Stannous Chloride Solution, 0.53M: Dissolve 50 g $SnCl_2$ into 250 mL 9N HCl solution.

7.17 Calibration Standards:

7.17.1 Stock Standard (100 mg/L): In an acid-rinsed, 1-L volumetric flask, dissolve 0.7491 g sodium sulfide nonahyrdate ($Na_2S \cdot 9H_2O$, Mallinckrodt 8044 or equivalent) in approximately 900 mL of 0.025 M sodium hydroxide reagent. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily. Standardize this stock standard after preparation.

7.17.1.1 In an acid rinsed, 250-mL Erlenmeyer flask, add 20 mL 0.0250 N iodine solution and 2 mL 1:1 HCl.

7.17.1.2 Add 10 mL of 100 mg/L stock standard.

7.17.1.3 Titrate with 0.0250 N sodium thiosulfate until a straw yellow color appears.

7.17.1.4 Add a few drops of 2% w/v starch indicator (mixture will turn blue) and continue titration until blue color disappears.

7.17.1.5 Calculate the concentration of stock standard using the following calculation

$$[((A \times B) - (C \times D)) \times 16000] / \text{mL sample} = \text{mg/L sulfide}$$

Where: A = normality of iodine solution

B = mL of iodine solution used

C = normality of thiosulfate solution

D = mL of thiosulfate used

7.17.1.6 Two blanks should be run to verify the normality of iodine and sodium thiosulfate has not changed.

7.17.1.7 Using the found concentration of the stock standard, determine the volume of stock standard needed to make the 10 mg/L intermediate standard. The formula used is $C_1V_1 = C_2V_2$.

7.17.2 Intermediate Stock Standard (10 mg/L): In an acid-rinsed 500-mL volumetric flask, add the volume of 100 mg/L stock standard determined in 7.14.1.7. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily.

7.17.3 Working Calibration Standards: To prepare 200 mL quantities of calibration standards, use acid-rinsed, 200-mL volumetric flasks. Add 20 mL of alkaline antioxidant reagent to approximately 100 mL of 0.025 M sodium hydroxide reagent. Use the table below to determine the correct amount of stock standard to pipette into each volumetric flask. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily.

Calibration Standard	Quantity of 10 mg/L Intermediate Stock Standard
2.0 mg/L	40 mL
1.0 mg/L	20 mL
0.50 mg/L	10 mL
0.1 mg/L	2 mL
0.05 mg/L	1 mL
0.02 mg/L	0.4 mL
0.01 mg/L	0.2 mL
0.0 mg/L	—

7.18 The second-source calibration verification (SCV) is purchased and prepared according to instructions provided by the manufacture. Use 0.025 M sodium hydroxide reagent as diluent and add alkaline antioxidant reagent at 10% of final volume.

7.19 1:1 Hydrochloric Acid: Add an equal volume of concentrated HCl (37%) to reagent water. This reagent is prepared by designated laboratory personnel and used to acid rinse glassware.

7.20 All reagents should be discarded if precipitate or growth appears.

7.21 All reagents and standards are verified as described in Section 9.6.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are collected in 125 mL glass serum bottles and stored at 4°C ± 2°C prior to analysis.

8.2 Bottle preservation and preparation

8.2.1 0.2 mL Zinc Acetate preservative, 0.5 mL sodium hydroxide (NaOH) preservative, and magnetic stir bar are added to each serum bottle.

8.2.2 Each bottle is purged with high purity nitrogen gas for 30 seconds and capped with a 20 mm septum stopper and a 20 mm tear off seal.

8.2.3 Each bottle is then weighed, using an analytical balance, and initial weight is recorded on label of bottle.

8.2.4 After samples are collected, bottles are weighed, using an analytical balance, and weight is recorded on label of bottle.

8.2.5 Using a Safety-Lok syringe, 5-6 mL of Alkaline Antioxidant Reagent is injected into each bottle.

8.2.6 Bottles are placed on stir plate, for at least 1 hour to dissolve any particulate.

8.2.7 Each bottle is weighed a 3rd time, using an analytical balance, and final weight is recorded on label of bottle.

8.2.8 All weights are recorded in Element bench sheet.

8.3 Maximum holding time is 14 days when stored at 4°C ± 2°C.

8.3.1 Holding time for Acid Volatiles is 6 months when preserved with Zinc Acetate and stored at -20 °C.

9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability (IDC): The analyst must be able to demonstrate that they can generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial Calibration: The 1st order calibration range must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument.

9.1.2 External Verification of Calibration: A second-source calibration verification standard (SCV) from an external source is analyzed. The results of the SCV must be within the manufacturer's certified range of the established SCV value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limit (MDL) Study: A minimum of 7 replicate Laboratory Control Samples (BS) are spiked at a value 1 to 5 times the estimated detection limit and processed over a period of three days. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated. Once the IDC has been established for this SOP, the Unit Supervisor may waive this requirement for individual analysts if the reference method does not specifically require an MDL study for new analysts.

9.1.4 Initial Precision and Accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.1.6 Demonstration of Low Background: Analyze at least one Method Blank (BLK) to determine reagent or laboratory contamination. The BLK result must meet the criteria established for the on-going demonstration of low background in Section 9.2.3.

9.1.7 Other Requirements for an IDC: An IDC may also be required if there are significant changes to the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis. Consult with the Quality Assurance Officer (QAO) to determine if any changes require an IDC.

9.1.8 IDC Documentation: An IDC for each analyst must be on file in the QA office along with an IDC for the method, matrix, and instrument.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily Calibration: Calibrate the instrument at the beginning of the analytical run or whenever the curve verification fails. Calibrate the instrument with a calibration blank and 7 standards covering the range of sample results and within the Linear Calibration Range (LCR) of the analyte. The curve used must be 2nd order polynomial and not forced through zero. Acceptable correlation coefficient for the calibration curve is 0.9990 or greater. The concentration of the calibration standards must be ±

10% of the true value, and ± 20% of the true value for the lowest standard. This corresponds to the percent residual calculation. The Calibration Statistics display on the analysis report summarizes in algebraic form what is seen graphically. The first equation shows the plotted calibration equation in the form of **Area f (Conc.)**, where the peak area is a function of **Conc.** or determined concentration of the analyte. The second equation is the same calibration equation, but solved for concentration. It is in the form **CONC = f (Area)**. This is the equation that is used to determine the concentration of unknowns. The third statistic is the value of **r**, the 'correlation coefficient' for the calibration.

9.2.2 External Verification of Calibration: Analyze a second source calibration verification (SCV) from the external source immediately after calibration to verify instrument performance. The results of the SCV must be within the manufacturer's range of the target value; otherwise corrective action is taken before analyzing samples. If the SCV is out of control, the run data can only be accepted by the Unit Supervisor.

9.2.3 Demonstration of Low Background: At the beginning of each run and with each batch, analyze an initial calibration blank (ICB) or blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK or ICB must be below the report level; otherwise the source of the contamination is investigated and corrected before samples are analyzed. Analyze a continuing calibration blank (CCB) every 10 samples and at the end of the run. The CCB must be less than the report level (MRL). If the CCB is above the Report Level, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Report Level Verification (RLV) Check: A Report Level Verification (CRL) check must be performed each time the instrument is calibrated. The CRL check is performed by

analyzing a calibration standard at or below the report level (0.01 mg/L). (The CRL check sample is not required to be processed through the entire SOP.) The percent recovery of the CRL must be within ± 40%.

9.2.4.1 If the percent recovery of the CRL is outside the acceptance criteria, the analyst must either: 1) repeat the CRL or 2) recalibrate and then perform the CRL. If the repeat CRL is within acceptance criteria, or if the instrument recalibration results in a CRL that is within acceptance criteria, the analyst may proceed with the analytical run. If the CRL is not within acceptance criteria, the analyst must either: 1) recalibrate the instrument and then perform the CRL once again, or 2) perform the CRL at a higher concentration level.

9.2.4.2 If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the Report Level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed CRL using the elevated Report Level until a new calibration curve and CRL meet the acceptance criteria.

9.2.5 Continuing Verification of Calibration: Analyze a continuing calibration verification standard (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.6 Accuracy: With every batch of 20 samples processed as a group, analyze a laboratory control sample (BS). Accuracy (as percent recovery) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Found Concentration of BS}}{\text{True Concentration of BS}} \times 100$$

9.2.7 If the recovery of the analyte falls outside the required control limits of 90-110%, the analyte is judged out of control. The source of the problem should be identified and the situation resolved before sample analysis can continue.

9.2.8 Matrix Effect: Run a matrix spike (MS) with each batch of 20 field samples processed as a group, or 5% of the samples analyzed, whichever is greater. The same solution used to fortify the BS is used to fortify the MS. Accuracy (as percent recovery after background correction) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Concentration of MS - Concentration of Matrix Sample}}{\text{True Concentration of MS}} \times 100$$

9.2.9 If the recovery of the MS falls outside of 80-120% limits, the MS is repeated. If the recovery of the repeat analysis also falls outside the control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the analyte still falls outside the designated MS recovery range and the BS, and ICV/CCV for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be matrix induced and the results for the diluted sample and the MS are reported using an elevated report level reflective of the dilution used and the qualifier QD: "Recovery in MS not within acceptance limits" is added to the MS.

9.2.7.1 If the MS recovery of the diluted sample is within acceptable limits, the sample is reported with an elevated Report Level reflective of the dilution used.

9.2.10 Precision: Analyze a laboratory duplicate (DUP) with each batch of field samples processed as a group, or10% of the field samples analyzed, whichever is greater. Calculations of the

absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.10.1 Calculate the relative percent difference of the duplicates using the following formula:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = concentration of sample

D = concentration of duplicate sample

9.2.10.2 Duplicate acceptance criteria:

Concentration Range	Criteria:
RL to 10xRL	None
10xRL to highest calibration std	RPD $\leq$ 10%

9.2.10.3 If the duplicate concentration is between the RL and 10xRL, and the RPD is greater than 10%, the qualifier QH is added to the duplicate: "RPD between sample duplicates not within acceptance limits. Analyte concentration in the samples too low for proper evaluation."

9.2.10.4 If the duplicate fails to meet the above criteria, the samples should be reanalyzed to verify poor duplicate analysis RPD. If the repeated duplicate is still not within acceptable limits, the samples must be reported with a qualifier identifying the sample analysis result as yielding poor duplicate analysis RPD.

9.3 External verification of laboratory performance: Proficiency Test (PT) samples are analyzed as required for Federal certification. If the results are not within acceptance criteria, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance Officer.

9.4 The MDL study is repeated when changes in instrumentation or instrument response occur. A minimum of 7 replicate Laboratory Fortified Blanks (LFB) or 7 Report Level Verification (CRL) checks are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3) MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Dissolved Analysis: The filtration blank results must be below the Report Level. If the filter blank is above the Report Level, consult with a lead worker or supervisor to determine if the filter blank result should be subtracted from the sample results or if other action should be taken.

9.6 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of ICV, ICB, SCV, CRL, CCV and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 7 calibration standards and a calibration blank by diluting suitable volumes of calibration standard solution, as described in Section 7.16.

10.2 Set up the manifold as shown in Section 17. If necessary, refer to the Lachat manual for instrument operation.

10.3 Process calibration standards and calibration blank and calibrate the instrument as described in Section 11. Read calibration standards and calibration blank in descending concentration on the Lachat.

10.4 Prepare calibration standard curve by plotting instrument response against concentration value. The curve used must be 2nd order polynomial and not

forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the Omnion® 3.0 Software. Attach a pdf of the curve to the sequence in Element to document the initial calibration. The calibration standard curve is accepted if a correlation coefficient of at least 0.9990 is achieved. Also the concentration of the standards must be within ± 10% of their true value except the lowest standard which can be ± 20% of its true value.

10.5 After the calibration has been established, it must be verified by the analysis of the ICV, ICB, SCV, CRL, CCV and CCB.

10.5.1 If measurements exceed ± 10% of the established ICV value (0.5 mg/L), the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.2 The background level of the analyte in the ICB must be at or below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed.

10.5.3 The results of the CRL must be within ± 40% of the true value (0.01 mg/L) in order to proceed. If it is not, follow the procedure outlined in Section 9.2.4.

10.5.4 If measurements exceed the range of the established SCV value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.5 A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) must be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 0.01 mg/L. The results for the calibration verification standard (CCV) must be within ± 10% of the true value (0.5 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

11.0 PROCEDURE

11.1 System Start-up

11.1.1 Set up manifold as shown in Section 17.2 and inspect manifold for proper connections.

11.1.2 Turn on power strip. Allow at least 15 minutes for the heating unit to warm up to 65°C. Do not pump reagents or water into the flow system until the temperature has reached 65°C.

11.1.3 Raise tension levers on pump tube cassettes. Place reagent lines into reagent water and check for leaks and smooth flow. Allow about 20 minutes for heater to reach equilibrium.

11.1.4 Transfer lines to designated reagent. Allow system to equilibrate until a stable baseline is achieved.

11.2 Prepare a BS and MS for each batch by adding 100 µL of Intermediate Stock Standard (10 mg/L) into a 10 mL borosilicate test tube. Add 5.0 mL of 0.0 mg/L blank solution or field sample. The true value is 0.2 mg/L.

11.3 Prepare a CRL by using the lowest non-zero standard, 0.01 mg/L. Pour approximately 5 mL of the 0.05 mg/L standard into a 10 mL borosilicate test tube.

11.4 Calibration and Sample Analysis

11.4.1 Prepare standards as described in Section 7.

11.4.2 Place calibration standards in descending order in the auto sampler standards tray. Select the default Sulfide template from the Sulfide data folder and input the information required by the data system, such as concentration, replicates, and QC scheme. Verify peak timing and integration parameters as specified in Section 17.3. Import the sequence ID numbers from Element Database.

11.4.3 Pour approximately 5 mL of each type of quality control and sample into a 10 mL borosilicate test tube and place in sample tray.

11.4.4 The CCV and CCB must be set up every 10 samples and at the end of each run in the template. The CCV is the 0.5 mg/L calibration standard. The CCB is the same as the calibration blank. The CCV and CCB come from the same cup as the equivalent calibration standard. Input the information required for the QC scheme. See Section 17.

11.4.5 Add approximately 5 mL of each properly preserved and prepared sample, filter blank, or sample aliquot diluted to 5 mL, into corresponding 10 mL borosilicate test tubes and place in sample tray. Set up 1 DUP for every 10 samples, and a BS and MS for every 20 samples.

11.4.5.1 After preservation and preparation, samples must be extracted from glass bottles using safety lock syringes. Discard locked syringe and needle in sharps container.

11.4.6 Calibrate the instrument by injecting standards. The data system will then associate the concentrations with the instrument responses for each standard and evaluate the curve.

11.4.7 After acceptable curve is achieved and initial QC is obtained and acceptable, continue with analysis.

11.5 System Shut Down

11.5.1 At the end of the run place all reagent lines into water to rinse for 15 minutes. Pump air through the manifold for 30 minutes to dry the distillation system, especially the membrane. Keep the heater at 65°C until 30 minutes of air drying is complete.

11.5.2 Turn off the pump and the power strip. Release the tension levers on the pump tube cassettes.

11.6 System and Procedure Notes

11.6.1 For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual (Guide is also available on request from Lachat). Consult the Instrument Book for the Lachat systems for current information on preventative maintenance procedures.

11.6.2 Samples that are over concentrated should be diluted with the diluent and not reagent water.

11.7 Acid-Volatile Samples

11.7.1 Allow samples to thaw to room temperature.

11.7.2 Using an analytical balance, weigh out 1 g of soil into Teflon vial. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors.

11.7.3 Add 25 mL Acid-volatile catch solution to each 50 mL trap and label each with specified sample number.

11.7.4 Set flow meters to a scale reading of 20. Loosely cap each Teflon vial and allow nitrogen to purge for at least three minutes.

11.7.5 Using a syringe, inject 15 mL stannous chloride solution into each Teflon vial. Quickly screwing on each cap so that no sulfide is lost.

11.7.6 Turn on stir plate and allow nitrogen to purge at room temperature for 3 hours.

11.7.7 After 3 hours remove 2.5 mL of sample and dilute with 2.5 mL of diluent and proceed to step 11.4.3.

11.8 Acid-Volatile dry weight

11.8.1 Allow samples to thaw to room temperature.

11.8.2 Tare the balance. Open the Acid-Volatile dry weight spreadsheet template. Enter dish numbers in spreadsheet. Open balance data transfer program and select Acid-Volatile method.

11.8.3 Place dish on balance. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors

11.8.4 ***When preparing Acid-Volatile solids it is essential that you mix the sample well.*** Using an analytical balance, weigh out 5 g of soil into. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors.

11.8.5 Set up a Duplicate (DUP) and for every 10 samples.

11.8.6 Place sample in 105° C for at least 12 hours. Remove dishes from oven using heat resistant gloves and tongs; allow dishes to cool on the bench top for no more than 10 minutes (set timer). Complete cooling to room temperature in desiccator.

11.8.7 Record dish weights using an analytical balance, computer, software and Excel spreadsheet enter dry weight in Element.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calibration is accomplished by injection of standards. The data system will then prepare a calibration curve by plotting instrument response versus standard concentration. Sample concentration is calculated from the regression equation. Multiply results by appropriate dilution factor.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file in the QA Office.

12.3 The minimum report level is 0.01 mg/L.

12.4 Results are reported in mg/L to three significant figures.

12.5 Sample results and quality control data are transferred electronically to the Element Database for review by the analyst.

12.6 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 2.0 mg/L are diluted and reanalyzed.

12.7 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

13.0 PERFORMANCE

13.1 Information pertinent to our laboratory's performance is available in the QA Office or Element.

13.2 Current MDL data are available in the QA Office.

13.3 Precision and accuracy data are available in the QA Office or Element.

14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult, "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C., 20036.

15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reduction, reclamation, recycling.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.

- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 For additional information regarding the laboratory's waste management policy, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

16.0 BIBLIOGRAPHY

16.1 Standard Methods for the Examination of Water and Wastewater. Method 4500-S^{2-}I and J. 21st Edition, On-line.

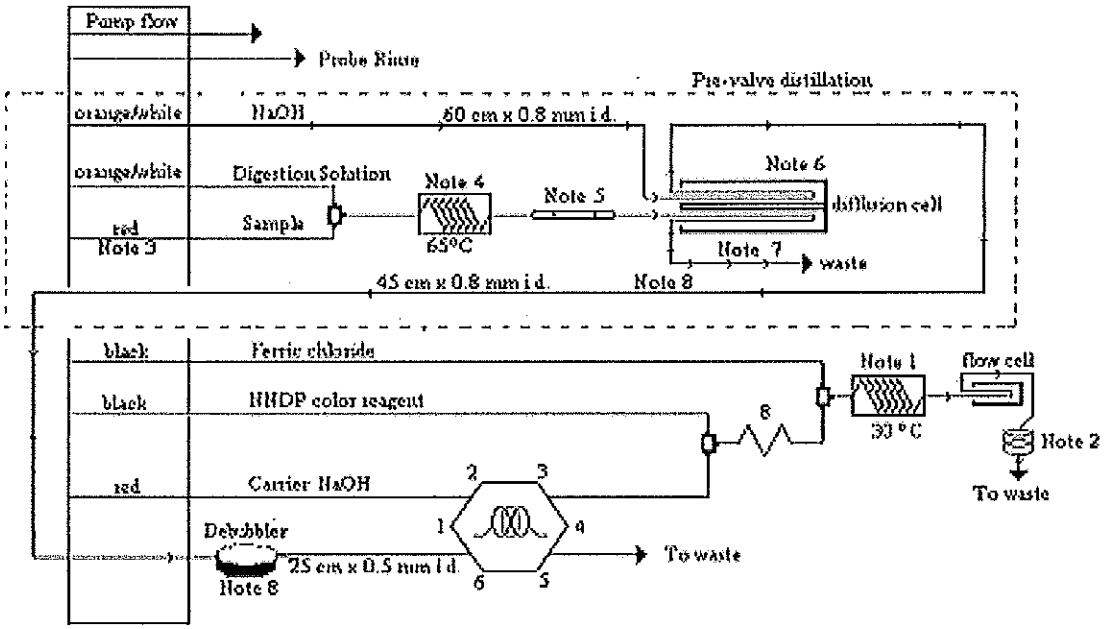
16.2 Lachat Instruments QuikChem® Method 10-116-29-3-A, Determination of Dissolved Sulfide by Flow Injection Analysis.

16.3 "Appendix B to Part 136-Definition and Procedure for the Determination of Method Detection Limit-Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

17.0 TABLES, FIGURES, VALIDATION DATA

17.1 The Initial Demonstration of Capability data are on file in the QA Office; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

17.2 Sulfide Manifold Diagram:



Carrier: 0.025 M NaOH (Reagent 5)
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 uL/cm.
AE Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.
QC8000 Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.

Interference Filter: 660 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows tubing wrapped around the heater block at the specified temperature; see manifold notes for the length of tubing used.

8: 168 cm of tubing on a 8 cm coil support

Note: PVC PUMP TUBES MUST BE USED FOR THIS METHOD

Note 1: 650 cm x 0.8 mm i.d. tubing wrapped on the heater at 30°C

Note 2: 200 cm x 0.5 mm i.d. backpressure loop

Note 3: The sample line is replaced with a red/red pump tube. 45 cm x.0.8 mm i.d. is used to connect the sample line to the mixing tee which merges with phosphoric acid.

Note 4: 1200 cm x 0.8 mm i.d. wrapped on the 65°C heater. The lengths of tubing on the heater inlet and outlet are 53 cm.

Note 5: The 53 cm lead of tubing from the outlet of the 65°C heater is covered with 52 cm of high temperature sleeving, (1/16" i.d., Lachat Part No. 50364) for heat insulation and then connected to the diffusion cell inlet on the bottom half.

Note 6: Diffusion cell (Lachat Part No. 50332) is mounted on the manifold board. The Donor (bottom) and Acceptor (top) streams flow in the same direction.

Note 7: To the diffusion cell outlet, bottom half, connect 100 cm x 0.8 mm i.d. manifold tubing plus a waste line (Lachat Part No. 50932)

Note 8: The Debubbler is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of the debubbler connected to Port 6 of the valve.

Note 9: One O-ring is installed on each of the flares provided with the diffusion cell. Then attach the tan fitting, and then a union is attached to each of the flared tubing's.

17.3 Quik Chem® 8000

17.3.1 The timing values listed below are approximate and may need to be optimized using graphical events programming.

Sample throughput:	60 samples/hour, 60 seconds/sample
Pump speed:	35
Cycle speed:	60

17.3.2 Analyte Data:

Concentration Units:	mg/L of NH_3 N
Expected Inject to Peak Start:	20 seconds
Expected Peak Base Width:	49 seconds
Chemistry:	Direct

17.3.3 Calibration Data:

Level	1	2	3	4	5	6	7
Concentration mg/L N	5.00	2.50	1.00	0.50	0.10	0.05	0.0

Calibration Fit Type:	1st Order Polynomial
Calibration Rep. Handling:	Average
Weighting Method:	None
Force through Zero:	No

17.3.4 Sampler Timing

Min. Probe in Wash Period:	5 seconds
Sample Period:	24 seconds

17.3.5 Valve Timing

Load Period:	15 seconds
Inject Period:	45 seconds
Time to Valve:	26 seconds

Approved By: _____ Date: 7/3/2013
Jeffrey Brenner, Inorganic Unit Supervisor

Approved By: _____ Date: 7/3/2013
Paul Moyer, Environmental Lab Section Manager

Appendix I

NPDES Equivalent Methods Do NOT Require Letter From USEPA

Lachat Instruments has received many questions regarding USEPA Equivalent methods for NPDES reporting. Many customers have requested letters from the EPA stating these methods' acceptance. Lachat would like to stress that the USEPA will not be issuing letters for methods that fall within the flexibility allowed at 40 CFR Part 136.6 of the EPA's Method Update Rule (MUR), March 2007, and that these methods **are acceptable** for NPDES compliance monitoring. A good example of this is Lachat method 10-107-04-1-C. Lachat Applications submitted the method for review to the USEPA, requesting a letter stating that the method was acceptable for use in both NPDWR and NPDES compliance monitoring. The modifications in this method allow samples to be analyzed without pH adjustment due to the high flow rate of the buffer reagent, which allows the method to compensate for high or low pH samples. This method adjustment falls within the flexibility allowed at 40 CFR Part 136.6 of the MUR. Therefore, this method is acceptable for use in NPDES compliance monitoring and no letter is required (or will be issued) by the EPA.

The EPA states that, ***"The absence of a letter does not preclude use of Equivalent Lachat methods for NPDES compliance monitoring purposes."*** The modifications that fall within the allowed flexibility of the MUR do not require review as a Clean Water Act ATP.

The USEPA sent Lachat and all Regional ATP Coordinators this statement regarding this issue:

"Due to increased inquiries on method flexibility we would like to stress:

Regions, States and permitting authorities should not expect a letter from the EPA's Office of Science and Technology (OST) stating that a modification that falls within the flexibility allowed under 40 CFR Part 136.6, which was added as part of the Methods Update Final Rule published in the Federal Register on March 12, 2007. Such modifications are acceptable for use in CWA monitoring. Letters for modified methods that fall within the scope of Part 136.6 will no longer be issued and the use of these methods are acceptable provided that they meet the performance requirements specified in the method.

Secondly, the flexibility allowed at Part 136.6 may be used to modify any method approved at Part 136 for compliance monitoring under the CWA including methods developed by VCSBs such as Standard Methods and ASTM International. If you choose to modify an approved method, in addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as Standard Methods, ASTM International or AOAC, International. This is further clarified in the attached memo from Richard Reding, Ph.D., Chief, EASB to Regional ATP Coordinators and Alternates titled: Citing Clean Water Act Limited-Use ATP Methods as Modifications dated April 14, 2008."

Please contact the EPA or Lachat Instruments for copies of the above-mentioned EPA correspondence.

EPA Contacts for MUR questions are:

CWA ATP Coordinator Lemuel Walker (walker.lemuel@epa.gov)

The CWA methods Team (OSTCWAMethods@epa.gov)

Lachat would love to hear about your lab's experiences with the MUR. Is the intent to allow for more flexibility helping your lab? Please send Lachat any comments, good or bad, on the MUR to Lachat Technical Support (support@lachatinstruments.com).

Appendix II

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

Date: April 14, 2008

To: Regional ATP Coordinators and Alternates

From: Richard Reding, Ph.D., Chief
Engineering and Analytical Support Branch
Engineering & Analysis Division, Office of Science & Technology

Topic: Citing Clean Water Act Limited-Use ATP Methods as Modifications

I am writing to our regional partners about citing a method for which a Region has issued a limited-use ATP approval letter that results in modifying another approved method. In addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as the Standard Methods Committee, AOAC, International, or ASTM, International.

For example, a lab with a CWA limited-use approval letter may conduct a luminescent measurement of dissolved oxygen (DO) with any approved method that requires a DO measurement, such as BOD or CBOD by SM5210B. However to do so, the lab will have a copy of a limited-use ATP approval letter. The lab SOP also will cite use of SM 5210B as "modified for luminescent measurement of DO in accordance with the limited-use ATP letter from the region" or similar wording.

Why do we recommend use of limited-use ATP approvals rather than wait for nation-wide approval? Because rulemaking can be a lengthy process. Thus in our national ATP letter, we recommend that regions consider approving use of the ATP under their limited-use ATP approval authority. Is it necessary for a limited-use ATP applicant to submit data, or do a side-by-side comparison in these cases? Our answer is generally no because methods that we review under the CWA ATP program already have multi-lab and comparability data.

Feel free to share this memo with your co-regulators, and the laboratory and method development community. Your contacts are the CWA ATP coordinator Lemuel Walker (walker.lemuel@epa.gov), or the CWA methods team (OSTCWAMethods@epa.gov).

cc: Lemuel Walker, CWA ATP coordinator
Steve Wendelken, SDWA ATP coordinator

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 25% Post-consumer)

Appendix D

University of Minnesota Duluth: Civil Engineering Laboratory – Standard Operating Procedures

Sulfide

DOC316.53.01136

USEPA[1] Methylene Blue Method[2] — Method 8131

(5 to 800 µg/L)

Scope and Application: For testing total sulfides, H_2S, HS^-, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA approved for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-S^{2-} D.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater.*

Test preparation

How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

Table 393 Instrument-specific information

Instrument	Sample volume	Sample cell	Cell orientation
DR 6000	10 mL	2495402	Fill line faces right
DR 5000	10 mL	2495402	Fill line faces user
DR 3900	10 mL	2495402	Fill line faces user
DR 3800, DR 2800, DR 2700	10 mL	2495402	Fill line faces right

Before starting the test:

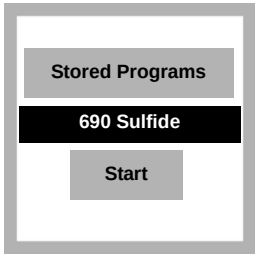
Analyze samples immediately. Do not preserve for later analysis.
Avoid excessive agitation of samples to minimize sulfide loss.
Some sulfide loss may occur if dilution is necessary.
Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration that is regulated as a hazardous waste by Federal RCRA. Refer to the current MSDS for safe handling and disposal instructions.

Collect the following items:

Description	Quantity
Sulfide 1 Reagent	1–2 mL
Sulfide 2 Reagent	1–2 mL
Water, deionized	10–25 mL
Pipet, serological, 10-mL	1
Pipet Filler, safety bulb	1
Sample Cells (see *Instrument-specific information*)	2
Stoppers	2

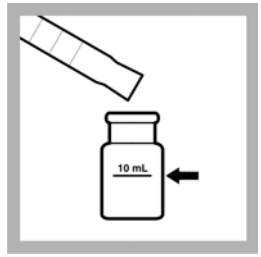
See *Consumables and replacement items* for reorder information.

Methylene Blue Method

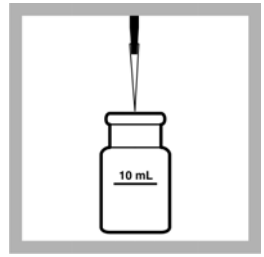


1. Select the test.

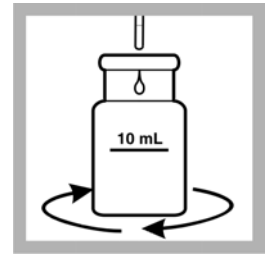
Insert an adapter if required (see *Instrument-specific information*). Refer to the user manual for orientation.



2. Blank Preparation: Measure 10 mL of deionized water in a sample cell.



3. Prepared Sample: Use a pipet to add 10 mL of sample to a second sample cell. Do not mix the sample more than necessary to prevent sulfide loss.



4. Use the dropper to add 0.5 mL Sulfide 1 Reagent to each cell.

Swirl to mix.

5. Use the dropper to add 0.5 mL Sulfide 2 Reagent to each cell.

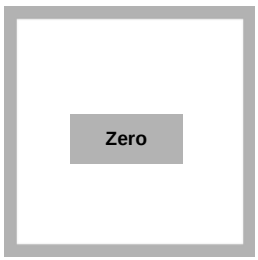
6. Cap or stopper the cell and immediately invert to mix.

The solution will turn pink initially and then turn blue if sulfide is present.

7. Start the instrument timer.

A five-minute reaction time will begin.

8. When the timer expires, wipe the blank and insert it in the cell holder.

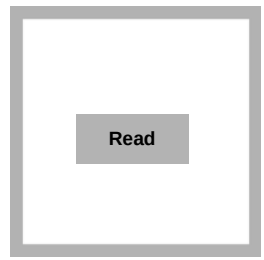


9. **ZERO** the instrument.

The display will show:

0.00 µg/L S^{2-}

10. Wipe the prepared sample and insert it in the cell holder.



11. **READ** the results in µg/L S^{2-}.

Soluble sulfides

Complete the following steps to measure soluble sulfides.

1. Centrifuge a sample in completely filled, capped tubes.
2. Use the supernatant in place of the sample and follow the *Methylene Blue Method* procedure.

To estimate insoluble sulfides, subtract the soluble sulfide concentration from the total sulfide concentration.

Interferences

Table 394 Interfering substances

Interfering substance	Interference level
Strong reducing substances such as sulfite, thiosulfate and hydrosulfite.	Interfere by reducing the blue color or preventing its development.
Sulfide, high levels	High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted.
Turbidity	For turbid samples, prepare a sulfide-free blank as follows. Use this blank in place of the deionized water blank in the *Methylene Blue Method* test procedure. 1. Measure 25 mL of sample into a 50-mL Erlenmeyer flask. 2. Add bromine water by drops with constant swirling until a permanent yellow color just appears. 3. Add phenol solution by drops until the yellow color just disappears. Use this solution to replace the deionized water in step 2 of the procedure. This pretreatment procedure removes sulfide from the sample, but the turbidity and any color will remain. The interference from turbidity or color will be corrected when the instrument is set to zero with this solution (step 9).

Sample collection, preservation and storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Prevent excessive shaking or prolonged exposure to air. Analyze samples immediately.

Method performance

Program	Instrument	Standard	Precision 95% Confidence Limits of Distribution	Sensitivity Concentration change per 0.010 Abs change
690	DR 5000	520 µg/L S^{2-}	504–536 µg/L S^{2-}	5µg/L S^{2-}

Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. Test results are measured at 665 nm.

Consumables and replacement items

Required reagents

Description	Quantity/Test	Unit	Catalog number
Sulfide Reagent Set, includes:	—	—	2244500
Sulfide 1 Reagent	1 mL	100 mL MDB	181632
Sulfide 2 Reagent	1 mL	100 mL MDB	181732
Water, deionized	10 mL	4 liters	27256

Required apparatus

Description	Quantity	Unit	Catalog number
Pipet, serological, 10-mL	1	each	53238
Pipet Filler, safety bulb	1	each	1465100
Stopper, for 18-mm Tube	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Catalog number
Bromine Water, 30 g/L	29 mL	221120
Phenol Solution, 30 g/L	29 mL	211220
Stopper, for 18-mm Tube	25/pkg	173125
Flask, Erlenmeyer, 50 mL	each	50541

FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

HACH COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

Appendix E

University of Minnesota Duluth: Dr. Nathan Johnson's "Peepers" Method Standard Operating Procedures

Peeper Sample Collection and Analysis

Standard Operating Procedure

Johnson Lab

Summer 2013

Revised: 6/24/2013

Table of Contents

Analyses for Peeper samples

This table outlines the details of the sample analyses for peeper porewater samples.

Large Cuvette Sample Size: ~4mL (down to 4.5) metals, 2.5mL sulfide, up to 1.25mL for iron, remainder (~1.5mL) for sulfate

Analyte	Vials	Pre-loaded reagents/mass	Sample to add	Post processing methods	Quantification
Metals (Zn, Cu, Fe)	6mL poly vial	N/A (just clean)	~4mL	measure pH immediately and acidify with 0.5% HNO3	ICP-MS
pH	In-situ or in metals bottle	N/A		Also measure pH in mud at two different depths (~2.5cm, 7.5cm)	Direct with pH meter
Sulfide (HS- + H2S)	6mL poly	Reagent 1 (5% or 125uL for 2.5 mL sample) (to be added the morning of)	2.5mL	Add reagent 2 (5% or 125uL for 2.5 mL sample) immediately after sample is added; weigh sample after	Spectrophotometer at 660 nm
Iron (Ferrous iron, 2+)	6mL poly vials	Reagent mix: 0.5mL DI water, 0.5mL phenanthroline, 0.25mL Acetate buffer, 0.025mL concentrated HCl	up to 1.25mL, 0.25mL at a time (stop when red color first appears)	Weigh sample after, add enough DI water to make 1.25mL of sample + dilution water	Spectrophotometer at 510 nm
Sulfate (SO4-2)	1.5mL amber poly vials	N/A (just clean)	Remainder of sample (~1.5mL)	Filter through iron cartridge into sample vial and acidify with HCl immediately; purge with N2 gas if evidence of sulfide	Ion Chromatography

Small Cuvette Sample Size: 1.5mL sulfide, 1.5mL sulfate, 1.5mL for iron, remainder for (1.5mL metals)

Some trouble was encountered for reproducibility with small volume cuvettes. As such, the small sample size should only be used for very high concentrations with expected absorbances of greater than 0.2 on the spectrophotometer.

Analyte	**Vials**	**Pre-loaded reagents/mass**	**Sample to add**	**Post processing methods**	**Quantification**
Metals (Zn, Cu, Fe)	20 mL Scint vials	N/A (just clean)	~4 mL (leave 5mL for other analyses)	measure pH (see below) and acidify with 0.5% HNO3	ICP-MS
pH	In-situ or in metals bottle	N/A		Also measure pH in mud at two different depths (~2.5cm, 7.5cm)	Direct with pH meter
Sulfide (HS- + H2S)	2mL vials	Reagent 1 (5% or 75uL for 1.5 mL sample) (to be added the morning of)	1.5mL	Add reagent 2 (5% or 75uL for 1.5 mL sample) immediately after sample is added; weigh sample after	Spectrophotometer at 660 nm
Iron (Ferrous iron, 2+)	20mL Scint vials	Reagent mix: 1mL DI water, 1mL phenanthroline, 0.5mL Acetate buffer,	up to 2.5mL, 0.5mL at a time (stop when red	Weigh sample after, add enough DI water to make 2.5mL	Spectrophotometer at 510 nm

		0.05mL concentrated HCl	color first appears)		
Sulfate (SO4-2)	2mL vials	N/A (just clean)	2mL (fill to brim or whatever is left)	Acidify with HCl immediately (or after measuring pH); purge with N2 gas	Ion Chromatography

Sulfide Calibration & Matrix spike

Stock preparation (in lab):

Prepare ~20x dilution of primary stock by degassing 4.75 mL of DI water +0.5 % 10 N NaOH for 15 minutes in 5 or 20 mL serum bottle. Carefully transport (minimizing splashing) to glovebox and add 0.25mL sulfide primary stock (typically ~37,000 uM) to degassed, alkaline working stock water. Cap and crimp in glove box.

Std	Vstd	Cstk	Vstk
0			
3.7 uM	5 mL	1850 uM	10 uL
7.4 uM	5 mL	1850 uM	20 uL
11.1 uM	5 mL	1850 uM	30 uL
Matrix spike	5 mL (in syringe)	1850 uM	20 uL (or appropriate volume 1-5x larger than expected sample concentration)

Blank (beginning of each peeper):

Prepare a blank **for each peeper** at the beginning of extraction using an unused bottom well and

7.5mL sample (triple preload Reagent 1). DO NOT ADD REAGENT 2.

Calibration (for each set of 2 peepers):
Prep 5mL sulfide standards during first peeper extraction using the volumes above and deaerated water used for peeper colection.

Matrix spike (once per trip):
extract 7.5mL from bottom well not being used for other analyses. use first 2.5mL exactly like any other sample. Spike volume in above table into extraction syringe barrel and gently mix. Dispense 2.5mL of spiked sample to each of Matrix Spike (MS) and Matrix Spike Duplicate (MSD) preloaded with reagent 1 and immediately add Reagent 2.

Iron Calibration & Matrix spike

Std	Vstd	Cstk	Vstk	
0				
30 uM	2.5mL	3000uM	25 uL	
60 uM	2.5mL	3000uM	50 uL	
180 uM	2.5mL	3000uM	150 uL	
Matrix spike	5mL	3000uM	600 uL	

Packing List:

- Paper towels
- Wash Basin (+ clean water if no on-site source)
- Props to hold peepers out of water
- 10ml syringes + needles
- Kim wipes (2 boxes)
- squirt bottles (x2)
- pre loaded, labeled and massed sample vials
- Notebook & pens & markers
- scissors, exacto knives
- labels

- gloves, safety glasses
- waste bottle, Sharps container
- extra bottles/vials/reagents
- DI water (1L)
- portable scale
- Spectrophotometer (& stock solutions)
- Cuvettes
- Split samples
- Pipette (1-20 uL & 100uL & 1mL)
- pipette tips
- pH meters (Field & lab) & calibration solution
- Beaker/electrode stand
- first aid kit
- Trash bag
- Batteries
- Iron filter
- HCl
- Nitric acid
- Phenanthroline
- Acetate Buffer
- Sulfide Reagent 1
- Sulfide Reagent 2
- Large Nitrogen bags, tank, regulator, tubing, wrench, tether strap, flow meter
- Table
- Tent, walls, clamps
- Buckets (at least 4 or 5)
- Cooler, Blue ice
- Bug spray, sunscreen

Additional Field supplies

- Diffuser
- Canoe, paddles, life jackets
- anchors and rope
- GPS Coordinates
- Extra nitrogen tank

- Jumbo Nitrogen Bags
- TP
- Knee boots or sandals
- Meals
- Rain gear
- (charged boat battery, power inverter, battery charger)

Field Deployment Packing list:

- Sealed peeper keeper
- Fence posts
- Nuts, bolts, washers
- Drive rod
- Canoe, paddles, life jackets
- Outriggers, anchor
- Rope
- Wrench
- Nitrogen tank, regulator, tubing, flow meter, tether strap
- Diffuser
- Nitrogen bags -- > jumbo
- Tray
- Extra DI water
- Peeper Keeper space fillers
- Press n Seal cling wrap
- Electrical tape
- Duct tape
- GPS coordinates
- Bug Spray
- Sunscreen
- Boots, Rain Gear
- Lunch

Procedure:

- Collect water from peeper wells (3 people required, minimum – one to handle sample vials, one to dry peeper wells and measure pH/acidify SO4 samples, one to draw sample from peeper wells and allocate to sample vials)
    - Fill rinse tub with water (does not need to be DI)
    - Assemble all materials necessary for upcoming steps in order to minimize time between peeper retrieval and placing samples in preserved sample vials
    - Remove peeper from sediment noting (with finger) which well is the first above the sediment water interface
    - Make note in lab notebook which well appeared to be the first above the S-W interface (based on finger method and based on visual observation of typical iron-oxide layer on first peeper well exposed to oxygenated overlying water). Write both down.
    - Submerge peeper in rinse tub and wipe excess mud off with kim-wipe (oxygen diffuses faster through air than water, so keeping peeper submerged in even oxygenated water minimizes oxygen intrusion).
    - Spray remaining sediment particles off with a squirt bottle filled with DI water. Remove as many particles as possible recognizing that the time required is a tradeoff between performing a thorough cleaning and introducing oxygen to peepers. I typically only spend ~5-10sec on each well to remove most loose particles. Some sediment particles will remain trapped between mesh and filter paper and it would take too long to try to get them all.
    - Place peeper into nitrogen filled plastic bag, seal bag (except for small vent hole) and purge with a slow stream of nitrogen to maintain positive pressure
    - Start extracting samples from peeper wells beginning with the most strongly reduced conditions and working your way towards progressively more oxidized conditions. Experience in sulfate-amended, high-organic mud has shown that the top 3-5cm of sediment has significant dissolved sulfide while deeper sediment has predominately dissolved iron. Wells in equilibrium with oxygenated overlying water can be sampled last.
        - Dry wells to be sampled first and the adjacent wells with several kimwipes to soak up water. Tipping the peeper slightly to one side while pressing a few kimwipes (balled up) against the mesh removes most water. Once the well to be sampled plus the two adjacent wells are fairly dry, sample extraction can commence.

        - With peeper tipped slightly to one side (to allow water to drain to needle) pierce bag+mesh+filter paper with 18g+ needle attached to syringe and position needle tip in the bottom corner of peeper well.
        - Ensure that water is not leaking into needle hole from the surface and place kimwipe on needle hole if necessary.
        - draw sample into syringe quickly (but not so quickly that a vacuum is formed in the barrel or significant splashing occurs) and stop filling immediately (or just before) air bubbles are seen (~8-9mL should be possible).
        - Allocate sample to pre-loaded sample vials.
            - First metals to brim (so that pH measurement is not compromised)
            - Secpmd sulfide
            - Third iron
            - Fourth sulfate
        - Minimize splashing during this process to preserve redox state of sample as much as possible and minimize the loss of dissolved gas (which can affect pH measurement).
        - Sample for sulfide analysis should be added as close as possible to the specified volume. Exact sample volume will be recorded based on mass back in lab so precise volume is not critical.
        - Sample for iron analysis should be added only until pink/red color appears in phenanthroline-loaded sample vials. Sample volume will be recorded based on mass back in lab so exact volume is not critical.
        - The remainder of the sample is used for pH and sulfate analysis. To avoid degassing of CO2 / H2S and consequent change in pH, care should be taken to minimize sample splashing/mixing while putting this last aliquot into a vial. Discharge below the solution surface and/or do not discharge sample fast & mix/agitate.
        - Change to new needle prior to extracting the next sample well
        - Move to next peeper well to be sampled (should already be dried) and extract next sample (again ensuring minimal water leaks into needle hole). Continue until all peeper wells have been completed.
    - As quickly as possible (within 1 minute), unpreserved samples for metals should be measured for pH (using fast-responding pH meter, rinsing/wiping between samples)
        - Measure pH with lab pH meter and record in lab notebook. Rinse probe with DI water between samples to minimize carryover between samples.
        - If accurate Cl measurements are necessary, an aliquot of sample for chloride

analysis should be removed prior to acidifying.

- As quickly as possible, sulfate sample should be acidified with HCl to convert all sulfide to volatile H2S prior to quantifying sulfate)
    - Add HCl to lower pH to <3. Experience has shown that ~0.1% (~1uL per mL sample) concentrated HCl is sufficient. Samples with excess H2S or CO3 could require additional acid.
    - Close vial and shake gently to mix in acid and partition H2S into headspace. Remove cap to let gaseous H2S evade. Either leave cap off or loosely cap to let sample continue to purge of H2S. Remember to tighten cap before transporting samples. Further active purging can take place in lab with a stream of N2.

Appendix F

Science of Museum of Minnesota – St. Croix Watershed Research Station (SCWRS) Laboratory Standard Operating Procedures

Extractable Metals SOP for Non-Point Source Sediments
8/6/98 D.R. Engstrom (Revised 02/27/2002 JC)

1. Dry sediments in freeze-drier; grind to a fine powder.

2. Make labels for 60ml acid-washed, PP bottles; record weight of bottle+ label.

3. In a dispenser bottle, make up 1L of 0.5N HCl from concentrated, high purity, HCl . Include lot # of acid on benchsheet. When making up acid, anything coming into contact with the acid must be *extremely* clean. Volumetric should be acid washed, triple rinsed with DI water, and rinsed with a small amount of high purity acid before using.

4. Weigh out 0.25 +/- 0.02 g dry sediment into a 50-ml, acid washed centrifuge tube on analytical balance; record exact weight.

4. Add 25ml high purity 0.5 N HCl using a dispenser bottle and record exact weight of acid used. Loosely cap vials and allow carbonates to react for a few minutes before proceeding. Include in set 10% duplicates and blanks of just 25ml HCl.

6. Heat in a hot-water bath at 80-85 degrees C for 30 minutes, plus time for samples to arrive at temperature (determine this using a thermometer in a water blank); place samples in refrigerator to stop reaction. Allow to cool 5 minutes.

7. Dry outside of tubes and centrifuge for 10 minutes at 1000 rpms (until solution is clear).

8. With an auto-pipettor, pipette 10.0 ml of sample supernatant into pre-weighed, 60ml, acid-washed, PP bottles; record solution weight.

9. Dilute sample solution with 40 +/- 0.5g DI H_2O on top-loading balance; record exact weight of water added.

Reagents

0.5 N high purity HCl
42g conc. HCl to 1.0 kg

Analytical

Analysis	Method	DF	Matrix	2nd Dilution
Trace Metals	ICP-MS	500	0.1 N HCl	none
Majors	ICP-MS	5000	0.01 N HCl	1:10

Table of Results

Sample No.	Vial No.	Sed. Wt.	HCl Wt.	Bottle Wt.	Extract Wt.	DI H2O Wt.

Notes

Include 250ml 0.5 N HCl lab to make up standards
Sample matrix will be 0.1 N HCl
Include 5-10% duplicates and blanks

Lachat analysis of aqueous sediment phosphorus extractions
0.01—2.0 mg P/L

(This SOP was developed by Kelly Thommes, SCWRS, in conjunction with Angela Craft-Reardon, Metropolitan Council, Environmental Services. It is modified from Lachat's Quikchem Method 10-115-01-1-A)

1. There are 3 phosphorus fractions to be analyzed for this set of extractions (plus a background color analysis for the NaOH-P fraction):
   1.1. Total P (TP) = Total phosphorus
   1.2. Apatite P (HCl-P) = Inorganic phosphorus (Ca-bound P)
   1.3. NAIP/Inorganic P (NaOH-P) = Non-apatite inorganic phosphorus (Al-P, Fe-P)

2. The analyst performing the sediment extractions should include 5-10% method duplicates, blanks, lab-fortified blanks, and spikes. Also, when selecting the HCl and NaOH samples for the method duplicates and spikes, it is helpful if the same sample is used for each fraction (i.e. if selecting sample A in the HCl fraction for a spike, select its counterpart in the NaOH fraction for that fraction's spike). This keeps confusion to a minimum when extracting the different fractions, pouring out samples prior to the Lachat analysis, and setting up trays in the Lachat software.

3. TP fraction (seems to be the most problematic for the Lachat)
   3.1. All TP fraction samples may possibly contain residual H2O2 from the extraction. Adding a small amount of sodium metabisulfite (Na2S2O5) to each sample neutralizes the H2O2. To correct for this dilution, one can either recalculate the Lachat results, or dilute the calibration standards by the same factor as the samples so the Lachat results are correct as they are output. We have successfully used the latter.
   3.2. The TP samples can display double peaks at low analyte concentrations. This may be a matrix effect due to changes in pH resulting from the addition of Na2S2O5.

   In order to make QA/QC calculations it is imperative to record weights for calibration standards, samples, spikes, and bisulfite additions for each QA/QC sample in each fraction.

Lachat Analysis

1. Prior to analysis, pour out 15mL (by weight) of each calibration standard.
2. Pipette 0.3mL of Na2S2O5 into each cal standard vial. Invert to mix.
3. The actual concentration of the calibration standards should be calculated accounting for the dilution. These values MUST be entered into the analyte table prior to running the calibration curve.
4. Run the calibration curve.
5. Pour out 6mL, by weight, of each sample in test tubes.

6. Pipette 0.12mL of $Na_2S_2O_5$ into each test tube. Invert to mix.
7. Make up a 0.5mg P/L check standard using Ampule 1 stock nutrient solution.
   7.1. The check standard can have $Na_2S_2O_5$ added to it in the same ratio as the samples and calibration standards (Measure 6mL of check standard into tube and add 0.12mL of $Na_2S_2O_5$. Invert to mix.). However, this may not be necessary.
8. Make up instrument spikes by pouring out 6mL of the intended spike sample, adding 0.12mL of 1 mg P/L phosphorus calibration standard to the spike, and then adding 0.12mL of $Na_2S_2O_5$. Invert several times to mix well.
9. Make up instrument Lab Fortified Blanks by following the procedure in step 8 using an extraction blank instead of sample.
10. Other QA/QC samples are as follows:
    10.1. Run a check standard at the beginning, middle, and end of a tray.
    10.2. Run a DI water blank before each check standard.
    10.3. Run at least 5-10% instrument duplicates at the end of each tray.

After the TP run, a new calibration curve must be run using fresh calibration standards. The HCl fractions and NaOH fractions do not have the extra bisulfite additions. After the second calibration curve is finished, run the HCl tray first, followed by the NaOH fraction. NO BISULFITE should be added to any of the HCl or NaOH samples, spikes, check standards, or lab-fortified blanks. However, the same general QA/QC procedures and guidelines should be followed (steps 8-10).

Once the HCl fraction is finished, run the NaOH fraction. If the QA/QC samples are the same for the two fractions (as recommended above), the Lachat tray file used for the HCl fraction may be used for the NaOH fraction.

The NaOH fraction samples have a yellow/brownish color to them, and it should be determined if this color being read by the Lachat detector. After the NaOH fraction is finished, pull the Lachat line out of the color reagent bottle and place it in the DI (carrier) bottle. Next rerun the NaOH tray to obtain background color/interference results. This set can be difficult for the software to integrate properly because the peaks are so small. Look for suspicious values such as numbers in the ten-thousandths range (e.g. 0.0006). Also, double check that each peak is integrated with a start and an end tick mark located properly about the peak. If a peak is not integrated properly, or has a suspicious result, then the analyst may need to rerun those samples (either by tacking them onto the end of a tray, or by rerunning them in a new run). If simply rerunning them does not fix the integration problems, then the Peak Base Width may need to be changed, the calibration curve reanalyzed with the new PBW changes, and the background tray reanalyzed under the new parameters.

Standard preparation

Dry ACS grade anhydrous potassium phosphate monobasic (KH_2PO_4) at 105 degrees C for at least one hour.

Stock Standard (250ppm P)
In a 1L volumetric dissolve1.099g KH_2PO_4 in approximately 800mL of DI water. Dilute to mark and invert to mix. Good for 6 months.

Working Stock Standard (20ppm P)
In a 1L volumetric dilute 80mL of stock standard to mark and invert to mix. Good for up to 6 months.

Set of 7 Working Standards
2.0 1.0 0.5 0.2 0.05 0.01 0.00 mg P/L

By Volume: To 6, 250mL volumetric flasks add
25 12.5 6.25 2.5 0.625 0.125 mL
of 20ppm working stock standard respectively (the 0.00ppm standard is fresh DI water). Dilute each working standard to the mark and invert to mix.

By weight: To 6, 250mL volumetric flasks add
25 12.5 6.25 2.5 0.625 0.125 g
of 20ppm working stock respectively (the 0.00ppm standard is fresh DI water). Record the exact weight of standard in each flask. To get the final weight of the solution after dilution, divide the exact weight of added standard by
0.1 0.05 0.025 0.01 0.0025 0.00005
respectively. Dilute each working standard up to its respective calculated weight with DI water.

Sediment Phosphorus Extraction Procedure
High Sample Throughput

Jan 12, 2010 D. R. Engstrom SCWRS

All Fractions

1. Freeze-dry and powder sediments.

Total-P

1. Weigh out 0.1 ± 0.01 g dry sediment into pre-weighed 50mL NUNC centrifuge tube on analytical balance; record exact weight of sediment.

2. In a fume hood: add 10 ml of 30% H_2O_2, and place in hot water bath (85-90°C); allow reaction to proceed one hour taking care that contents do not boil out during the early stages of the reaction (use stream of MeOH to control bubbles).

3. Remove samples from heat and bring weight to 30 g with d-H_2O on top-loading balance; add 10 ml of 2.0 N HCl and return to hot water bath for 30 min.

4. Cool samples in cold water bath and record final weight on top-loading balance; centrifuge for 10 minutes at 3500 rpm.

5. Pipette 5.0 ml of extract with pipet into pre-weighed 60-ml pp. bottle; record extract weight and dilute to 50 g with d-H_2O on top-loading balance; label with sample number and code **TP**.

6. Add 6.25 mL of 1 M $Na_2S_2O_5$ (sodium meta bisulfite) to each bottle. Record weight added.

Ex-P

(The two exchangeable-P extracts can be combined one bottle—use 2.5 mL aliquots from each extraction period instead of 5 mL and dilute to 50 g final weight with DI water)

1. Weigh out second aliquot of 0.1± 0.02 g dry sediment into labeled, pre-weighed 50-ml centrifuge tube on analytical balance; record exact weight of sediment.

2. Label two 60 mL PP bottles for each sample, one set with code **Ex-P 1st** and the other with **Ex-P 2nd** (or label one bottle **Ex-P** if combining aliquots)

3. Add 40 mL of 1 M NH_4Cl to centrifuge tube and record total weight. Cap tubes tightly.

4. Shake on shaker tray for 2 hours at 120 RPM. Position tubes so that sediment is disturbed during shaking.

5. Centrifuge for 10 minutes at 3500 RPM.

6. Pipette 5 mL of supernatant into a pre-labeled, Ex-P 1st 60 mL PP bottle. Record weight of extract.

7. Bring weight extract weight to 50 g with d-H_2O and record final solution weight.

8. Sip off remaining supernatant in centrifuge tube with sipper and vacuum pump taking care that no sediment is lost.

9. Repeat steps 2-7 for a second extraction this time using the Ex-P 2nd bottles.

10. Add ca. 25 ml d-H_2O, swirl contents and centrifuge for 10 min; remove supernatant with vacuum "sipper" and discard.

NaOH-P

1. Using sediment already extracted with NH_4Cl add 25 ml of 0.1 M NaOH and record total weight; cap tubes tightly and shake for 16 hr at room temp on rotary shaker 120 RPM.

2. Centrifuge for 10 minutes at 3500 rpm.

3. Pipette 5.0 ml of extract with pipet into pre-weighed 60-ml pp. bottle; record extract weight and dilute to 50 g with d-H_2O on top-loading balance; label with sample number and code **NaOH-P**.

4. Drain as much remaining supernatant from centrifuge tube with a vacuum "sipper" into waste container, taking care that no sediment is lost.

5. Add ca. 25 ml d-H_2O, swirl contents and centrifuge for 10 min; again remove supernatant with vacuum "sipper".

HCl-P

1. Bring contents of centrifuge tube containing residual sediment to 18.75 g with d-H_2O water on top-loading balance.

2. Add 6.25 ml 2.0 N HCl; cap tubes tightly and shake on rotary shaker for 20 hr at room temp. (Keep shaker RPMs at highest level that does not cause sample to slosh at top of centrifuge tube—only need to keep sediment lightly agitated.)

3. Centrifuge for 10 minutes at 3500 rpm.

4. Pipette 5.0 ml of solution with pipet into pre-weighed 60-ml pp. bottle; record solution weight and dilute to 50 g with d-H_2O on top-loading balance; label with sample number and code **HCl-P**.

Reagents

1. 30% (low-P) hydrogen peroxide H_2O_2

2. 1 M NH_4Cl
   53.5 g NH_4C dissolved in 1 L DI

3. 0.1 M sodium hydroxide NaOH
   4 g solid NaOH to 1 L

4. 2.0 N hydrochloric acid HCl
   165 mL conc. HCl to 1 L

5. 1.0 M sodium metabisulfite $Na_2S_2O_5$
   19.01 g solid $Na_2S_2O_5$ to 100 g DI

Analytical

Analysis	Method	DF	Expected Conc.	Matrix
Total-P	Ascorbic Acid	2500	400 ppb	0.05 M HCl
NaOH-P	Ascorbic Acid	2500	200 ppb	0.01 M NaOH
HCl-P	Ascorbic Acid	2500	80 ppb	0.05 M HCl

Phosphorus Analysis

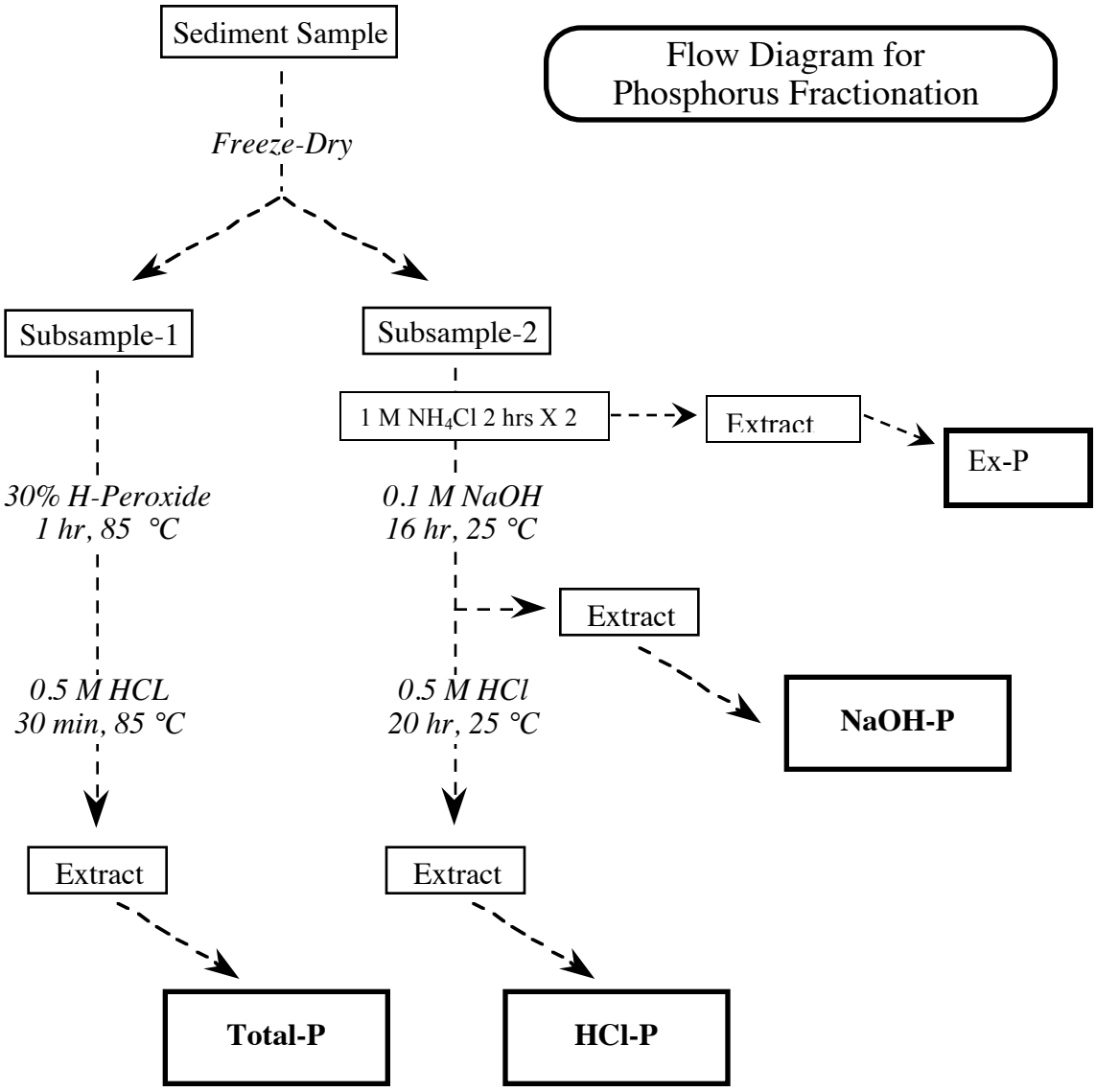
- Analyze on a Lachat QuikChem 8000 using method QuikChem method 10-115-01-1A

- use 5-cm flow-through cell (200 ppb = ca. 0.4 Abs)

- standards for all fractions (0, 10, 50, 200, 500, 1000, 2000 ppb)

- spike Total-P samples (50 ml) and standards with 6.25 ml of 1 M $Na_2S_2O_5$ prior to addition of color reagent to remove any remaining peroxide

- split NaOH-P fraction into two 50-ml aliquots; add complete color reagent to one aliquot and color reagent w/o ascorbic acid to the other; read the second aliquot as background correction for absorbance from extracted DOC.



Ex-P represents exchangeable-P

NaOH-P (NAIP) represents Fe/Al-bound P

HCl Extractable-P (Apatite-P) represents Ca-bound P

Residual-P (Organic-P) = Total-P – (NaOH-P + HCl-P)

Appendix G

Gustavus Adolphus College Chemistry Department Laboratory – Standard Operating Procedures

INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-µg/L concentrations of a large number of elements in water samples and in waste extracts or digests (Refs. 1 and 2). When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-soluble) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of this method in a multi-laboratory study on solid and aqueous wastes are listed below.

Element		CASRN[a]
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Nickel	(Ni)	7440-02-0

Element		CASRN[a]
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Sodium	(Na)	7440-23-5
Thallium	(Tl)	7440-28-0
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Chemical Abstract Service Registry Number

Acceptability of this method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectrophotometry or inductively coupled plasma-atomic emission spectrometry. It should be noted that one multi-laboratory study was conducted in 1988 and advances in ICP-MS instrumentation and software have been made since that time and additional studies have been added with validation and improvements in performance of the method. Performance, in general, exceeds the multi-laboratory performance data for the listed elements. It is expected that current performance will exceed the multi-laboratory performance data for the listed elements (and others) that are provided in Sec. 13.0. The lower limit of quantitation and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, quantitation limits will generally be below 0.1 µg/L. Less sensitive elements (like Se and As) and desensitized major elements may be 1.0 µg/L or higher.

1.3 If this method is used to determine any analyte not listed in Sec. 1.2, it is the responsibility of the analyst to demonstrate the accuracy and precision of the method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Sec. 9.0). Other elements and matrices may be analyzed by this method if performance is demonstrated for the analyte of interest, in the matrices of interest, at the concentration levels of interest in the same manner as the listed elements and matrices (see Sec. 9.0).

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, ^{74}Ge, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant native amounts of the recommended internal standards.

1.5 Prior to employing this method, analysts are advised to consult the each preparative method that may be employed in the overall analysis (e.g., a 3000 series method) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.6 Use of this method is restricted to use by, or under supervision of, properly experienced and trained personnel, including spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples should be solubilized or digested using the appropriate sample preparation methods (see Chapter Three). When analyzing groundwater or other aqueous samples for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis (refer to Sec. 1.1).

2.2 This method describes the multi-elemental determination of analytes by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced by high temperatures are entrained in the plasma gas and extracted through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 DEFINITIONS

Refer to Chapter One, Chapter Three, and the manufacturer's instructions for definitions that may be applicable to this procedure.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method to be used for specific guidance on quality control procedures and to Chapter Three for general guidance on the cleaning of glassware. Also refer to the preparative methods to be used for discussions on interferences.

4.2 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isotope, or use of another method.

4.3 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature (Refs. 3 and 4). Examples include $^{75}ArCl^+$ ion on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature (Ref. 5), the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting statistics. Because the ^{35}Cl natural abundance of 75.77% is 3.13 times the ^{37}Cl abundance of 24.23%, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06% of the $^{40}Ar^{35}Cl^+$ signal):

Corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
(m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal),

where the final term adjusts for any selenium contribution at 77 m/z.

NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [Ref. 6]).

Similarly:

Corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =
(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal),

where last 2 terms adjust for any $^{114}Sn^+$ or $^{114}MoO^+$ contributions at m/z 114.

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients could be improved. The most appropriate coefficients for a particular instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1%) counting precision.

The accuracy of these types of equations is based upon the constancy of the observed isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found (Ref. 7) to be reliable, e.g., oxide levels can vary with operating conditions. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferent. For example, this type of correction has been reported (Ref. 7) for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed gas plasmas have been shown to greatly reduce molecular interferences (Ref. 8). These techniques can be used provided that the lower limits of quantitation, accuracy, and precision requirements for analysis of the samples can be met.

4.4 Additionally, solid phase chelation may be used to eliminate isobaric interferences from both element and molecular sources. An on-line method has been demonstrated for environmental waters such as sea water, drinking water and acid decomposed samples. Acid decomposed samples refer to samples decomposed by methods similar to Methods 3052, 3051, 3050 or 3015. Samples with percent levels of iron and aluminum should be avoided. The

method also provides a method for preconcentration to enhance quantitation limits simultaneously with elimination of isobaric interferences. The method relies on chelating resins such as imminodiacetate or other appropriate resins and selectively concentrates the elements of interest while eliminating interfering elements from the sample matrix. By eliminating the elements that are direct isobaric interferences or those that form isobaric interfering molecular masses, the mass region is simplified and these interferences can not occur. The method has been proven effective for the certification of standard reference materials and validated using SRMs (Refs. 13 through 15). The method has the potential to be used on-line or off-line as an effective sample preparation method specifically designed to address interference problems.

4.5 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement (Ref. 9). Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) are recommended (Ref. 10) to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes (Ref. 11). When intolerable physical interferences are present in a sample, a significant suppression of the internal standard signals (to less than 30% of the signals in the calibrations standard) will be observed. Dilution of the sample fivefold (1+4) will usually eliminate the problem (see Sec. 9.5).

4.6 Memory interferences or carry-over can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of observed memory interferences. The rinse period between samples must be long enough to eliminate significant memory interference.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

5.2 Concentrated nitric and hydrochloric acids are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a hood and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection when working with these reagents. Hydrofluoric acid is a very toxic acid and penetrates the skin and tissues deeply if not treated immediately. Injury occurs in two stages; first, by hydration that induces tissue necrosis and then by penetration of fluoride ions deep into the tissue and by reaction with calcium. Boric acid and other complexing reagents and appropriate treatment agents should be administered immediately. Consult appropriate safety literature and have the appropriate treatment materials readily available prior to working with this acid. See Method 3052 for specific suggestions for handling hydrofluoric acid from a safety and an instrument standpoint.

5.3 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

5.4 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. For this reason, the acidification and digestion of samples should be performed in an approved fume hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma-mass spectrometer -- A system capable of providing resolution, better than or equal to 1.0 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution is recommended.

6.2 Argon gas supply -- High-purity grade (99.99%).

7.0 REAGENTS AND STANDARDS

7.1 Reagent- or trace metals-grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2% (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed when hydrochloric and sulfuric acids are used (Refs. 3 and 4). Concentrations of antimony and silver between 50-500 µg/L require 1% (v/v) HCl for stability; for concentrations above 500 µg/L Ag, additional HCl will be needed. Consequently, accuracy of analytes requiring significant chloride molecular ion corrections (such as As and V) will degrade.

7.3 Reagent water -- All references to water in the method refer to reagent water, unless otherwise specified. Reagent water must be free of interferences.

7.4 Standard stock solutions for each analyte may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010 for instructions on preparing standard solutions from solids.

7.4.1 Bismuth internal standard stock solution (1 mL = 100 µg of Bi) -- Dissolve 0.1115 g of Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.2 Germanium internal standard stock solution (1 mL = 100 µg of Ge) -- Dissolve 0.2954 g of $GeCl_4$ in a minimum amount of dilute HNO_3. Add 10 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.3 Holmium internal standard stock solution (1 mL = 100 µg of Ho) -- Dissolve 0.1757 g of $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.4 Indium internal standard stock solution (1 mL = 100 µg of In) -- Dissolve 0.1000 g of indium metal in 10 mL of conc. HNO_3. Dilute to 1,000 mL with reagent water.

7.4.5 Lithium internal standard stock solution (1 mL = 100 µg of ^6Li) -- Dissolve 0.6312 g of 95-atom-% ^6Li, Li_2CO_3 in 10 mL of reagent water and 10 mL of HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.6 Rhodium internal standard stock solution (1 mL = 100 µg of Rh) -- Dissolve 0.3593 g of ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL of conc. HCl and dilute to 1,000 mL with reagent water.

7.4.7 Scandium internal standard stock solution (1 mL = 100 µg of Sc) -- Dissolve 0.15343 g of Sc_2O_3 in 10 mL (1+1) of hot HNO_3. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.8 Terbium internal standard stock solution (1 mL = 100 µg of Tb) -- Dissolve 0.1828 g of $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) of HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL of conc. HNO_3 and dilute to 1,000 mL with reagent water.

7.4.9 Yttrium internal standard stock solution (1 mL = 100 µg of Y) -- Dissolve 0.2316 g of $Y_2(CO_3)_3 \cdot 3H_2O$ in 10 mL (1+1) of HNO_3. Add 5 mL conc. of HNO_3 and dilute to 1,000 mL with reagent water.

7.4.10 Titanium interference stock solution (1 mL = 100 µg of Ti) -- Dissolve 0.4133 g of $(NH_4)_2TiF_6$ in reagent water. Add 2 drops of conc. HF and dilute to 1,000 mL with reagent water.

7.4.11 Molybdenum interference stock solution (1 mL = 100 µg of Mo) -- Dissolve 0.2043 g of $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

7.4.12 Gold preservative stock solution for mercury (1 mL = 100 µg) -- Recommend purchasing as high purity prepared solution of $AuCl_3$ in dilute hydrochloric acid matrix.

7.5 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1% (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, ^{74}Ge and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. For all intermediate and working standards, especially low level standards (i.e., <1 ppm), stability must be demonstrated prior to use. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. (Refer to Sec. 10.3.1 for guidance on determining the viability of standards.)

7.6 Blanks -- Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The method blank is used to monitor for

possible contamination resulting from either the reagents (acids) or the equipment used during sample processing including filtration. The rinse blank is used to flush the system between all samples and standards.

7.6.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1% HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Sec. 7.2.

7.6.2 The method blank must contain all of the reagents in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis (refer to Sec. 9.9).

7.6.3 The rinse blank consists of 1 to 2% of HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples. If mercury is to be analyzed, the rinse blank should also contain 2 µg/mL (ppm) of $AuCl_3$ solution.

7.7 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

NOTE: The final ICS solution concentrations in Table 1 are intended to evaluate corrections for known interferences on only the analytes in Sec. 1.2. If this method is used to determine an element not listed in Sec. 1.2, the analyst should modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see Sec. 9.7).

7.7.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

7.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g of $Al(NO_3)_3$·9H_2O, 2.498 g of $CaCO_3$ (dried at 180 EC for 1 hr before weighing), 1.000 g of Fe, 1.658 g of MgO, 2.305 g of Na_2CO_3, and 1.767 g of K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

7.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g of 85 % H_3PO_4, 6.373 g of 96% H_2SO_4, 40.024 g of 37% HCl, and 10.664 g of citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

7.7.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-µg/mL arsenic, cadmium, selenium, chromium, cobalt, copper, manganese, nickel, silver, vanadium, and zinc stock solutions to about 50 mL of

reagent water. Add 2.0 mL of concentrated HNO_3, and dilute to 100.0 mL with reagent water.

7.7.1.4 Working ICS solutions

7.7.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), and 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

7.7.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (Sec. 7.7.1.1), 2.0 mL each of 100-µg/mL titanium stock solution (Sec. 7.4.9) and molybdenum stock solution (Sec. 7.4.10), 5.0 mL of mixed ICS solution II (Sec. 7.7.1.2), and 2.0 mL of mixed ICS solution III (Sec. 7.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

7.8 The initial calibration verification (ICV) standard is prepared by the analyst (or a purchased second source reference material) by combining compatible elements from a standard source different from that of the calibration standard, and at concentration near the midpoint of the calibration curve (see Sec. 10.4.3 for use). This standard may also be purchased.

7.9 The continuing calibration verification (CCV) standard should be prepared in the same acid matrix using the same standards used for calibration, at a concentration near the mid-point of the calibration curve (see Sec. 10.4.4 for use).

7.10 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 µg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Sec. 10.2). This solution is also used to verify that the instrument has reached thermal stability (see Sec. 11.4).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 See the introductory material in Chapter Three, "Inorganic Analytes."

8.2 Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in this method.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technique-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection.

9.2 Refer to a 3000 series method (Method 3005, 3010, 3015, 3031, 3040, 3050, 3051, or 3052) for appropriate QC procedures to ensure the proper operation of the various sample preparation techniques.

9.3 Instrument detection limits (IDLs) are a useful tool to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limits of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 10.2.3.

IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months or at a project-specific designated frequency and kept with the instrument log book. Refer to Chapter One for additional guidance.

9.4 Initial demonstration of proficiency

Each laboratory must demonstrate initial proficiency with each sample preparation (a 3000 series method) and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. If an autosampler is used to perform sample dilutions, before using the autosampler to dilute samples, the laboratory should satisfy itself that those dilutions are of equivalent or better accuracy than is achieved by an experienced analyst performing manual dilutions. The laboratory must also repeat the demonstration of proficiency whenever new staff members are trained or significant changes in instrumentation are made.

9.5 Dilute and reanalyze samples that exceed the linear dynamic range or use an alternate, less sensitive calibration for which quality control data are already established.

9.6 The intensities of all internal standards must be monitored for every analysis. If the intensity of any internal standard in a sample falls below 70% of the intensity of that internal standard in the initial calibration standard, a significant matrix effect must be suspected. As an example, if the initial calibration internal standard response is 100,000 cps, anything below 70,000 cps in the sample would be unacceptable. Under these conditions, the established lower limit of quantitation has degraded and the correction ability of the internal standardization technique becomes questionable. The following procedure is followed -- First, make sure the instrument has not drifted by observing the internal standard intensities in the nearest clean matrix (calibration blank, Sec. 7.6.1). If the low internal standard intensities are also seen in the nearest calibration blank, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples. If drift has not occurred, matrix effects need to be removed by dilution of the affected sample. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. If the first dilution does not eliminate the problem, this procedure must be repeated until the internal-standard intensities rise to the minimum 70% limit. Reported results must be corrected for all dilutions.

9.7 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. For example, tungsten oxide moleculars can be very difficult to distinguish from mercury isotopes. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correction equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Sec. 4.2) for each instrument system are acceptable corrections for use in Method 6020.

9.8 For each batch of samples processed, at least one method blank must be carried throughout the entire sample preparation and analytical process, as described in Chapter One. A method blank is prepared by using a volume or weight of reagent water at the volume or weight specified in the preparation method, and then carried through the appropriate steps of the analytical process. These steps may include, but are not limited to, prefiltering, digestion, dilution, filtering, and analysis. If the method blank does not contain target analytes at a level that interferes with the project-specific DQOs, then the method blank would be considered acceptable.

In the absence of project-specific DQOs, if the blank is less than 10% of the lower limit of quantitation check sample concentration, less than 10% of the regulatory limit, or less than 10% of the lowest sample concentration for each analyte in a given preparation batch, whichever is greater, then the method blank is considered acceptable. If the method blank cannot be considered acceptable, the method blank should be re-run once, and if still unacceptable, then all samples after the last acceptable method blank should be reprepared and reanalyzed along with the other appropriate batch QC samples. These blanks will be useful in determining if samples are being contaminated. If the method blank exceeds the criteria, but the samples are all either below the reporting level or below the applicable action level or other DQOs, then the sample data may be used despite the contamination of the method blank.

9.9 Laboratory control sample (LCS)

For each batch of samples processed, at least one LCS must be carried throughout the entire sample preparation and analytical process. The laboratory control samples should be spiked with each analyte of interest at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory derived limit developed through the use of historical analyses. In the absence of project-specific or historical data generated criteria, this limit should be set at ± 20% of the spiked value. Acceptance limits derived from historical data should be no wider that ± 20%. If the laboratory control sample is not acceptable, then the laboratory control sample should be re-run once and,

if still unacceptable, all samples after the last acceptable laboratory control sample should be reprepared and reanalyzed.

Concurrent analyses of standard reference materials (SRMs) containing known amounts of analytes in the media of interest are recommended and may be used as an LCS. For solid SRMs, 80 - 120% accuracy may not be achievable and the manufacturer's established acceptance criterion should be used for soil SRMs.

9.10 Matrix spike, unspiked duplicate, or matrix spike duplicate (MS/Dup or MS/MSD)

Documenting the effect of the matrix, for a given preparation batch consisting of similar sample characteristics, should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch or as noted in the project-specific planning documents. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

For each batch of samples processed, at least one MS/Dup or MS/MSD sample set should be carried throughout the entire sample preparation and analytical process as described in Chapter One. MS/MSDs are intralaboratory split samples spiked with identical concentrations of each analyte of interest. The spiking occurs prior to sample preparation and analysis. An MS/Dup or MS/MSD is used to document the bias and precision of a method in a given sample matrix.

Refer to Chapter One for definitions of bias and precision, and for the proper data reduction protocols. MS/MSD samples should be spiked at the same level, and with the same spiking material, as the corresponding laboratory control sample that is at the project-specific action level or, when lacking project-specific action levels, at approximately mid-point of the linear dynamic range. Acceptance criteria should either be defined in the project-specifc planning documents or set at a laboratory-derived limit developed through the use of historical analyses per matrix type analyzed. In the absence of project-specific or historical data generated criteria, these limits should be set at ± 25% of the spiked value for accuracy and 20 relative percent difference (RPD) for precision. Acceptance limits derived from historical data should be no wider that ± 25% for accuracy and 20% for precision. Refer to Chapter One for additional guidance. If the bias and precision indicators are outside the laboratory control limits, if the percent recovery is less than 75% or greater than 125%, or if the relative percent difference is greater than 20%, then the interference test discussed in Sec. 9.11 should be conducted.

9.10.1 The relative percent difference between spiked matrix duplicate or unspiked duplicate determinations is to be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{\left(\frac{|D_1 + D_2|}{2}\right)} \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.
D_2 = second sample value (spiked or unspiked duplicate).

9.10.2 The spiked sample or spiked duplicate sample recovery should be within ± 25% of the actual value, or within the documented historical acceptance limits for each matrix.

9.11 If less than acceptable accuracy and precision data are generated, additional quality control tests (Secs. 9.11.1 and 9.11.2) are recommended prior to reporting concentration data for the elements in this method. At a minimum these tests should be performed with each batch of samples prepared/analyzed with corresponding unacceptable data quality results. These test will then serve to ensure that neither positive nor negative interferences are affecting the measurement of any of the elements or distorting the accuracy of the reported values. If matrix effects are confirmed, the laboratory should consult with the data user when feasible for possible corrective actions which may include the use of alternative or modified test procedures so that the analysis is not impacted by the same interference.

9.11.1 Post digestion spike addition

If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise another sample from the same preparation should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. If this spike fails, then the dilution test (Sec. 9.11.2) should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.11.2 Dilution test

If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should agree within ± 10% of the original determination. If not, then a chemical or physical interference effect should be suspected.

9.12 Ultra-trace analysis requires the use of clean chemistry preparation and analysis techniques. Several suggestions for minimizing analytical blank contamination are provided in Chapter Three.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Set up the instrument with proper operating parameters established as detailed below. The instrument should be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration). For operating conditions, the analyst should follow the instructions provided by the instrument manufacturer.

10.2 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10% peak height.

10.2.1 Before using this procedure to analyze samples, data should be available documenting the initial demonstration of performance. The required data should document the determination of the linear dynamic ranges; a demonstration of the desired method sensitivity and instrument detection limits; and the determination and verification of the appropriate correction equations or other routines for correcting spectral interferences. These data should be generated using the same instrument, operating conditions, and calibration routine to be used for sample analysis. These data should be kept on file and be available for review by the data user or auditor.

10.2.2 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference corrections need to be established for each individual target analyte on each particular instrument. All measurements (both target analytes and constituents which interfere with the target analytes) need to be within the instrument linear range where the correction equations are valid.

10.2.3 The lower limits of quantitation should be established for all isotope masses utilized for each type of matrix analyzed and for each preparation method used and for each instrument. These limits are considered the lowest reliable laboratory reporting concentrations and should be established from the lower limit of quantitation check sample and then confirmed using either the lowest calibration point or from a low-level calibration check standard.

10.2.3.1 Lower limit of quantitation check sample

The lower limit of quantitation check (LLQC) sample should be analyzed after establishing the lower laboratory reporting limits and on an as needed basis to demonstrate the desired detection capability. Ideally, this check sample and the low-level calibration verification standard will be prepared at the same concentrations with the only difference being the LLQC sample is carried through the entire preparation and analytical procedure. Lower limits of quantitation are verified when all analytes in the LLQC sample are detected within ± 30% of their true value. This check should be used to both establish and confirm the lowest quantitation limit.

10.2.3.2 The lower limits of quantitation determination using reagent water represents a best case situation and does not represent possible matrix effects of real-world samples. For the application of lower limits of quantitation on a project-specific basis with established data quality objectives, low-level matrix-specific spike studies may provide data users with a more reliable indication of the actual method sensitivity and minimum detection capabilities.

10.2.4 Specific recommended isotopes for the analytes noted in Sec. 1.2 are provided in Table 2. Other isotopes may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. Because of differences among various makes and models of mass spectrometers, specific instrument operating conditions cannot be provided. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality for the specific project and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a given task.

10.3 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are listed in Table 2.

10.4 All analyses require that a calibration curve be prepared to cover the appropriate concentration range based on the intended application and prior to establishing the linear dynamic range. Usually, this means the preparation of a calibration blank and mixed calibration standard solutions (Sec. 7.5), the highest of which would not exceed the anticipated linear dynamic range of the instrument. Check the instrument standardization by analyzing appropriate QC samples as follows.

10.4.1 Individual or mixed calibration standards should be prepared from known primary stock standards every six months to one year as needed based on the concentration stability as confirmed from the ICV analyses. The analysis of the ICV, which is prepared from a source independent of the calibration standards, is necessary to verify the instrument performance once the system has been calibrated for the desired target analytes. It is recommended that the ICV solution be obtained commercially as a certified traceable reference material such that an expiration date can be assigned. Alternately, the ICV solution can be prepared from an independent source on an as needed basis depending on the ability to meet the calibration verification criteria. If the ICV analysis is outside of the acceptance criteria, at a minimum the calibration standards must be prepared fresh and the instrument recalibrated prior to beginning sample analyses. Consideration should also be given to preparing fresh ICV standards if the new calibration cannot be verified using the existing ICV standard.

NOTE: This method describes the use of both a low-level and mid-level ICV standard analysis. For purposes of verifying the initial calibration, only the mid-level ICV needs to be prepared from a source other than the calibration standards.

10.4.1.1 The calibration standards should be prepared using the same type of acid or combination of acids and at similar concentrations as will result in the samples following processing.

10.4.1.2 The response of the calibration blank should be less than the response of the typical laboratory lower limit of quantitation for each desired target analyte. Additionally, if the calibration blank response or continuing calibration blank verification is used to calculate a theoretical concentration, this value should be less than the level of acceptable blank contamination as specified in the approved quality assurance project planning documents. If this is not the case, the reason for the out-of-control condition must be found and corrected, and the sample analyses may not proceed or the previous ten samples need to be reanalyzed.

10.4.2 For the initial and daily instrument operation, calibrate the system according to the instrument manufacturer's guidelines using the mixed calibration standards as noted in Sec. 7.5. The calibration curve should be prepared daily with a minimum of a calibration blank and a single standard at the appropriate concentration to effectively outline the desired quantitation range. Flush the system with the rinse blank (Sec. 7.6.3) between each standard solution. Use the average of at least three integrations for both calibration and sample analyses. The resulting curve should then be verified with mid-level and low-level initial calibration verification standards as outlined in Sec. 10.4.3.

Alternatively, the calibration curve can be prepared daily with a minimum of a calibration blank and three non-zero standards that effectively bracket the desired sample concentration range. If low-level as compared to mid- or high-level sample concentrations are expected, the calibration standards should be prepared at the appropriate concentrations in order to demonstrate the instrument linearity within the anticipated

sample concentration range. For all multi-point calibration scenarios, the lowest non-zero standard concentration should be considered the lower limit of quantitation.

NOTE: Regardless of whether the instrument is calibrated using only a minimum number of standards or with a multi-point curve, the upper limit of the quantitation range may exceed the highest concentration calibration point and can be defined as the "linear dynamic" range, while the lower limit can be identified as the "lower limit of quantitation limit" (LLQL) and will be either the concentration of the lowest calibration standard (for multi-point curves) or the concentration of the low level ICV/CCV check standard. Results reported outside these limits would not be recommended unless they are qualified as estimated. See Sec. 10.4.4 for recommendations on how to determine the linear dynamic range, while the guidance in this section and Sec. 10.4.3 provide options for defining the lower limit of quantitation.

10.4.2.1 To be considered acceptable, the calibration curve should have a correlation coefficient greater than or equal to 0.998. When using a multi-point calibration curve approach, every effort should be made to attain an acceptable correlation coefficient based on a linear response for each desired target analyte. If the recommended linear response cannot be attained using a minimum of three non-zero calibration standards, consideration should be given to adding more standards, particularly at the lower concentrations, in order to better define the linear range and the lower limit of quantitation. Conversely, the extreme upper and lower calibration points may be removed from the multi-point curve as long as three non-zero points remain such that the linear range is narrowed and the non-linear upper and/or lower portions are removed. As with the single point calibration option, the multi-point calibration should be verified with both a mid- and low-level ICV standard analysis using the same 90 - 110% and 70 - 130% acceptance criteria, respectively.

10.4.2.2 Many instrument software packages allow multi-point calibration curves to be "forced" through zero. It is acceptable to use this feature, provided that the resulting calibration meets the acceptance criteria, and can be verified by acceptable QC results. Forcing a regression through zero should NOT be used as a rationale for reporting results below the calibration range defined by the lowest standard in the calibration curve.

10.4.3 After initial calibration, the calibration curve should be verified by use of an initial calibration verification (ICV) standard analysis. At a minimum, the ICV standard should be prepared from an independent (second source) material at or near the mid-range of the calibration curve. The acceptance criteria for this mid-range ICV standard should be ±10% of its true value. Additionally, a low-level initial calibration verification (LLICV) standard should be prepared, using the same source as the calibration standards, at a concentration expected to be the lower limit of quantitation. The suggested acceptance criteria for the LLICV is ±30% of its true value. Quantitative sample analyses should not proceed for those analytes that fail the second source standard initial calibration verification, with the exception that analyses may continue for those analytes that fail the criteria with an understanding these results should be qualified and would be considered estimated values. Once the calibration acceptance criteria is met, either the lowest calibration standard or the LLICV concentration can be used to demonstrate the lower limit of quantitation and sample results should not be quantitated below this lowest standard. In some cases depending on the stated project data quality objectives, it may be appropriate to report these results as estimated, however, they should be qualified by noting the results are below the lower limit of quantitation. Therefore, the laboratory's

quantitation limit cannot be reported lower than either the LLICV standard used for the single point calibration option or the low calibration and/or verification standard used during initial multi-point calibration. If the calibration curve cannot be verified within these specified limits for the mid-range ICV and LLICV analyses, the cause needs to be determined and the instrument recalibrated before samples are analyzed. The analysis data for the initial calibration verification analyses should be kept on file with the sample analysis data.

10.4.4 Both the single and multi-point calibration curves should be verified at the end of each analysis batch and after every 10 samples by use of a continuing calibration verification (CCV) standard and a continuing calibration blank (CCB). The CCV should be made from the same material as the initial calibration standards at or near the mid-range concentration. For the curve to be considered valid, the acceptance criteria for the CCV standard should be ±10% of its true value and the CCB should contain target analytes less than the established lower limit of quantitation for any desired target analyte. If the calibration cannot be verified within the specified limits, the sample analysis must be discontinued, the cause determined and the instrument recalibrated. All samples following the last acceptable CCV/CCB must be reanalyzed. The analysis data for the CCV/CCB should be kept on file with the sample analysis data.

The low level continuing calibration verification (LLCCV) standard should also be analyzed at the end of each analysis batch. A more frequent LLCCV analysis, i.e., every 10 samples may be necessary if low-level sample concentrations are anticipated and the system stability at low end of the calibration is questionable. In addition, the analysis of a LLCCV on a more frequent basis will minimize the number of samples for re-analysis should the LLCCV fail if only run at the end of the analysis batch. The LLCCV standard should be made from the same source as the initial calibration standards at the established lower limit of quantitation as reported by the laboratory. The acceptance criteria for the LLCCV standard should be ± 30% of its true value. If the calibration cannot be verified within these specified limits, the analysis of samples containing the affected analytes at similar concentrations cannot continue until the cause is determined and the LLCCV standard successfully analyzed. The instrument may need to be recalibrated or the lower limit of quantitation adjusted to a concentration that will ensure a compliant LLCCV analysis. The analysis data for the LLCCV standard should be kept on file with the sample analysis data.

10.5 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hr, whichever is more frequent. Do this by analyzing the interference check solutions A and AB. The analyst should be aware that precipitation from solution AB may occur with some elements, specifically silver. Refer to Sec. 4.0 for a discussion on interferences and potential solutions to those interferences if additional guidance is needed.

NOTE: Analysts have noted improved performance in calibration stability if the instrument is exposed to the interference check solution after cleaning sampler and skimmer cones. Improved performance is also realized if the instrument is allowed to rinse for 5 or 10 min before the calibration blank is run.

10.6 The linear dynamic range is established when the system is first setup, or whenever significant instrument components have been replaced or repaired, and on an as needed basis only after the system has been successfully calibrated using either the single or multi-point standard calibration approach.

The upper limit of the linear dynamic range needs to be established for each wavelength utilized by determining the signal responses from a minimum of three, preferably five, different concentration standards across the range. The ranges which may be used for the analysis of samples should be judged by the analyst from the resulting data. The data, calculations and rationale for the choice of range made should be documented and kept on file. A standard at the upper limit should be prepared, analyzed and quantitated against the normal calibration curve. The calculated value should be within 10% (±10%) of the true value. New upper range limits should be determined whenever there is a significant change in instrument response. At a minimum, the range should be checked every six months. The analyst should be aware that if an analyte that is present above its upper range limit is used to apply a spectral correction, the correction may not be valid and those analytes where the spectral correction has been applied may be inaccurately reported.

NOTE: Some metals may exhibit non-linear response curves due to ionization and self-absorption effects. These curves may be used if the instrument allows it; however the effective range must be checked and the second order curve fit should have a correlation coefficient of 0.998 or better. Third order fits are not acceptable. These non-linear response curves should be revalidated and/or recalculated on a daily basis using the same calibration verification QC checks as a linear calibration curve. Since these curves are much more sensitive to changes in operating conditions than the linear lines, they should be checked whenever there have been moderate equipment changes. Under these calibration conditions, quantitation is not acceptable above or below the calibration standards. Additionally, a non-linear curve should be further verified by calculating the actual recovery of each calibration standard used in the curve. The acceptance criteria for the calibration standard recovery should be ±10% of its true value for all standards except the lowest concentration. A recovery of ±30% of its true value should be achieved for the lowest concentration standard.

10.7 The analyst should (1) verify that the instrument configuration and operating conditions satisfy the project-specific analytical requirements and (2) maintain quality control data that demonstrate and confirm the instrument performance for the reported analytical results.

11.0 PROCEDURE

11.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Groundwater and other aqueous samples designated for a dissolved metals determination which have been prefiltered and acidified will not need acid digestion. However, all associated QC samples (i.e., method blank, LCS and MS/MSD) must undergo the same filtration and acidification procedures. Samples which are not digested must be matrix-matched with the standards. Solubilization and digestion procedures are presented in Chapter Three, "Inorganic Analytes."

CAUTION: If mercury is to be analyzed, the digestion procedure must use mixed nitric and hydrochloric acids through all steps of the digestion. Mercury will be lost if the sample is digested when hydrochloric acid is not present. If it has not already been added to the sample as a preservative, Au should be added to give a final concentration of 2 mg/L (use 2.0 mL of 7.4.12 per 100 mL of sample) to preserve the mercury and to prevent it from plating out in the sample introduction system.

11.2 Initiate appropriate operating configuration of the instrument’s computer according to the instrument manufacturer's instructions.

11.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

11.4 Operating conditions -- The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 min for the instrument to equilibrate before analyzing any samples. This must be verified by an analysis of the tuning solution (Sec. 7.10) at least four integrations with relative standard deviations of #5% for the analytes contained in the tuning solution.

CAUTION: The instrument should have features that protect itself from high ion currents. If not, precautions must be taken to protect the detector from high ion currents. A channel electron multiplier or active film multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

11.5 Calibrate the instrument following the procedure outlined in Sec. 10.0.

11.6 Flush the system with the rinse blank solution (Sec. 7.6.3) until the signal levels return to the DQO or method's levels of quantitation (usually about 30 sec) before the analysis of each sample (see Sec. 10.0). Nebulize each sample until a steady-state signal is achieved (usually about 30 sec) prior to collecting data. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

11.7 Regardless of whether the initial calibration is performed using a single high standard and the calibration blank or the multi-point option, the laboratory should analyze an LLCCV (Sec. 10.4.4). For all analytes and determinations, the laboratory must analyze an ICV and LLICV (Sec. 10.4.3) immediately following daily calibration. It is recommended that a CCV LLCCV, and CCB (Sec. 10.4.4) be analyzed after every ten samples and at the end of the analysis batch.

11.8 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate but less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 10.2 and 10.4). Alternatively apply solid phase chelation chromatography to eliminate the matrix as described in Sec. 4.4.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 The quantitative values must be reported in appropriate units, such as micrograms per liter (µg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values. All results should be reported with up to three significant figures.

12.2 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations must include appropriate interference corrections (see Sec. 4.2 for examples), internal-standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

12.3 Results must be reported in units commensurate with their intended use and all dilutions must be taken into account when computing final results.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 In an EPA multi-laboratory study (Ref. 12), twelve laboratories applied the ICP-MS technique to both aqueous and solid samples. Table 3 summarizes the method performance data for aqueous samples. Performance data for solid samples are provided in Table 4. These data are provided for guidance purposes only.

13.3 Table 5 summarizes the method performance data for aqueous and sea water samples with interfering elements removed and samples preconcentrated prior to analysis. Table 6 summarizes the performance data for a simulated drinking water standard. These data are provided for guidance purposes only.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, http://www.acs.org.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. G. Horlick, et al., Spectrochim. Acta 40B, 1555 (1985).

2. A. L. Gray, Spectrochim. Acta 40B, 1525 (1985); 41B, 151 (1986).

3. S. H. Tan and G. Horlick, Appl. Spectrosc. 40, 445 (1986).

4. M. A. Vaughan and G. Horlick, Appl. Spectrosc. 40, 434 (1986).

5. N. E. Holden, "Table of the Isotopes," in D. R. Lide, Ed., CRC Handbook of Chemistry and Physics, 74th Ed., CRC Press, Boca Raton, FL, 1993.

6. T. A. Hinners, E. Heithmar, E. Rissmann, and D. Smith, Winter Conference on Plasma Spectrochemistry, Abstract THP18; p. 237, San Diego, CA (1994).

7. F. E. Lichte, et al., Anal. Chem. 59, 1150 (1987).

8. E. H. Evans and L. Ebdon, J. Anal. At. Spectrom. 4, 299 (1989).

9. D. Beauchemin, et al., Spectrochim. Acta 42B, 467 (1987).

10. R. S. Houk, Anal. Chem. 58, 97A (1986).

11. J. J. Thompson and R. S. Houk, Appl. Spectrosc. 41, 801 (1987).

12. W. R. Newberry, L. C. Butler, M. L. Hurd, G. A. Laing, M. A. Stapanian, K. A. Aleckson, K.A., D. E. Dobb, J. T. Rowan, J.T., and F. C. Garner, "Final Report of the Multi-Laboratory Evaluation of Method 6020 CLP-M Inductively Coupled Plasma-Mass Spectrometry" (1989).

13. Daniel B. Taylor, H. M. Kingston, D. J. Nogay, D. Koller, and R. Hutton, "On-Line Solid-phase Chelation for the Determination of Eight Metals in Environmental Waters by Inductively Coupled Plasma Mass Spectrometry."

14. H. M. Kingston, A. Siriraks, and J. M. Riviello, Patent Number 5,126,272, "A Method and Apparatus for Detecting Transition and Rare Earth Elements in a Matrix," U.S. Patent, Filed

U.S. Patent Office, March 1989, 31 pages, Granted June 30, 1992, Patent held by US Government.

15. H. M. Kingston, A. Siriraks, and J. M. Riviello, Patent Number 5,244,634 , "A Method and Apparatus for Detecting Transition and Rare Earth Elements in a Matrix," U.S. Patent, Filed U.S. Patent Office, March 1989, 31 pages, Granted Sept. 14, 1993, Patent held by US Government.

16. D. E. Dobb, J. T. Rowan, and D. Cardenas, Lockheed Environmental Systems and Technologies Co., Las Vegas, NV; and L. C. Butler, and E. M. Heithmar, E.M., U.S.EPA, Las Vegas, NV; "Determination of Mercury by ICP-MS."

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution Component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	100.0	100.0
Ca	300.0	300.0
Fe	250.0	250.0
Mg	100.0	100.0
Na	250.0	250.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	2000.0	2000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.100
Cd	0.0	0.100
Cr	0.0	0.200
Co	0.0	0.200
Cu	0.0	0.200
Mn	0.0	0.200
Hg	0.0	0.020
Ni	0.0	0.200
Se	0.0	0.100
Ag	0.0	0.050
V	0.0	0.200
Zn	0.0	0.100

These data are provided for guidance purposes only.

TABLE 2
RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Element of Interest	Mass(es)
Aluminum	**27**
Antimony	121, **123**
Arsenic	**75**
Barium	138, 137, 136, **135**, 134
Beryllium	**9**
Bismuth (IS)	209
Cadmium	**114**, 112, **111**, 110, 113, 116, 106
Calcium (I)	42, 43, **44**, 46, 48
Chlorine (I)	35, 37, (77, 82)[a]
Chromium	**52**, **53**, **50**, 54
Cobalt	**59**
Copper	**63**, **65**
Germanium (IS)	74
Holmium (IS)	165
Indium (IS)	**115**, 113
Iron (I)	**56**, **54**, **57**, 58
Lanthanum (I)	139
Lead	**208**, **207**, **206**, 204
Lithium (IS)	6[b], 7
Magnesium (I)	24, **25**, **26**
Manganese	**55**
Mercury	202, **200**, 199, 201
Molybdenum (I)	98, 96, 92, **97**, 94, (108)[a]
Nickel	58, **60**, 62, **61**, 64
Potassium (I)	**39**
Rhodium (IS)	103
Scandium (IS)	45
Selenium	80, **78**, **82**, **76**, **77**, 74
Silver	**107**, **109**
Sodium (I)	**23**
Terbium (IS)	159
Thallium	**205**, 203
Vanadium	**51**, **50**
Tin (I)	120, **118**
Yttrium (IS)	89
Zinc	64, **66**, **68**, **67**, 70

[a] These masses are also useful for interference correction (Sec. 4.2).
[b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

NOTE: Method 6020 is recommended for only those analytes listed in Sec.1.2. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes.

TABLE 3

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	16 - 16	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique (ICP-AES or GFAA).

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). A larger number gives a more reliable comparison.

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 4

EXAMPLE ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	19 - 34	15 - 16	7
Beryllium	50 - 87	8.6 - 14	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

Data obtained from Ref. 12.

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique.

[b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value).

[c] S is the number of samples with results greater than the limit of quantitation.

[d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

These data are provided for guidance purposes only.

TABLE 5

EXAMPLE METHOD PERFORMANCE DATA FOR AQUEOUS AND SEA WATER SAMPLES[A]
WITH INTERFERING ELEMENTS REMOVED
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]		
		9.0 mL	27.0 mL	CERTFIED
Manganese	55	1.8±0.05	1.9±0.2	1.99±0.15
Nickel	58	0.32±0.018	0.32±0.04	0.30±0.04
Cobalt	59	0.033±0.002	0.028±0.003	0.025±0.006
Copper	63	0.68±0.03	0.63±0.03	0.68±0.04
Zinc	64	1.6±0.05	1.8±0.15	1.97±0.12
Copper	65	0.67±0.03	0.6±0.05	0.68±0.04
Zinc	66	1.6±0.06	1.8±0.2	1.97±0.12
Cadmium	112	0.020±0.0015	0.019±0.0018	0.019±0.004
Cadmium	114	0.020±0.0009	0.019±0.002	0.019±0.004
Lead	206	0.013±0.0009	0.019±0.0011	0.019±0.006
Lead	207	0.014±0.0005	0.019±0.004	0.019±0.006
Lead	208	0.014±0.0006	0.019±0.002	0.019±0.006

Data obtained from Ref. 12.
[A] The dilution of the sea-water during the adjustment of pH produced 10 mL samples containing 9 mL of sea-water and 30 mL samples containing 27 mL of sea-water. Samples containing 9.0 mL of CASS-2, n=5; samples containing 27.0 mL of CASS-2, n=3.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

TABLE 6

ANALYSIS OF NIST SRM 1643b, TRACE METALS IN WATER[A]
AND SAMPLES PRECONCENTRATED PRIOR TO ANALYSIS

ELEMENT	ISOTOPE	CONCENTRATION (ng/mL)[B]	
		DETERMINED	CERTFIED
Manganese	55	30±1.3	28±2
Nickel	58	50±2	49±3
Cobalt	59	27±1.3	26±1
Nickel	60	51±2	49±3
Copper	63	23±1.0	21.9±0.4
Zinc	64	67±1.4	66±2
Copper	65	22±0.9	21.9±0.4
Zinc	66	67±1.8	66±2
Cadmium	111	20±0.5	20±1
Cadmium	112	19.9±0.3	20±1
Cadmium	114	19.8±0.4	20±1
Lead	206	23±0.5	23.7±0.7
Lead	207	23.9±0.4	23.7±0.7
Lead	208	24.2±0.4	23.7±0.7

Data obtained from Ref. 12.

[A] 5.0 mL samples, n=5.
[B] Concentration (ng/mL) ± 95% confidence limits.

These data are provided for guidance purposes only.

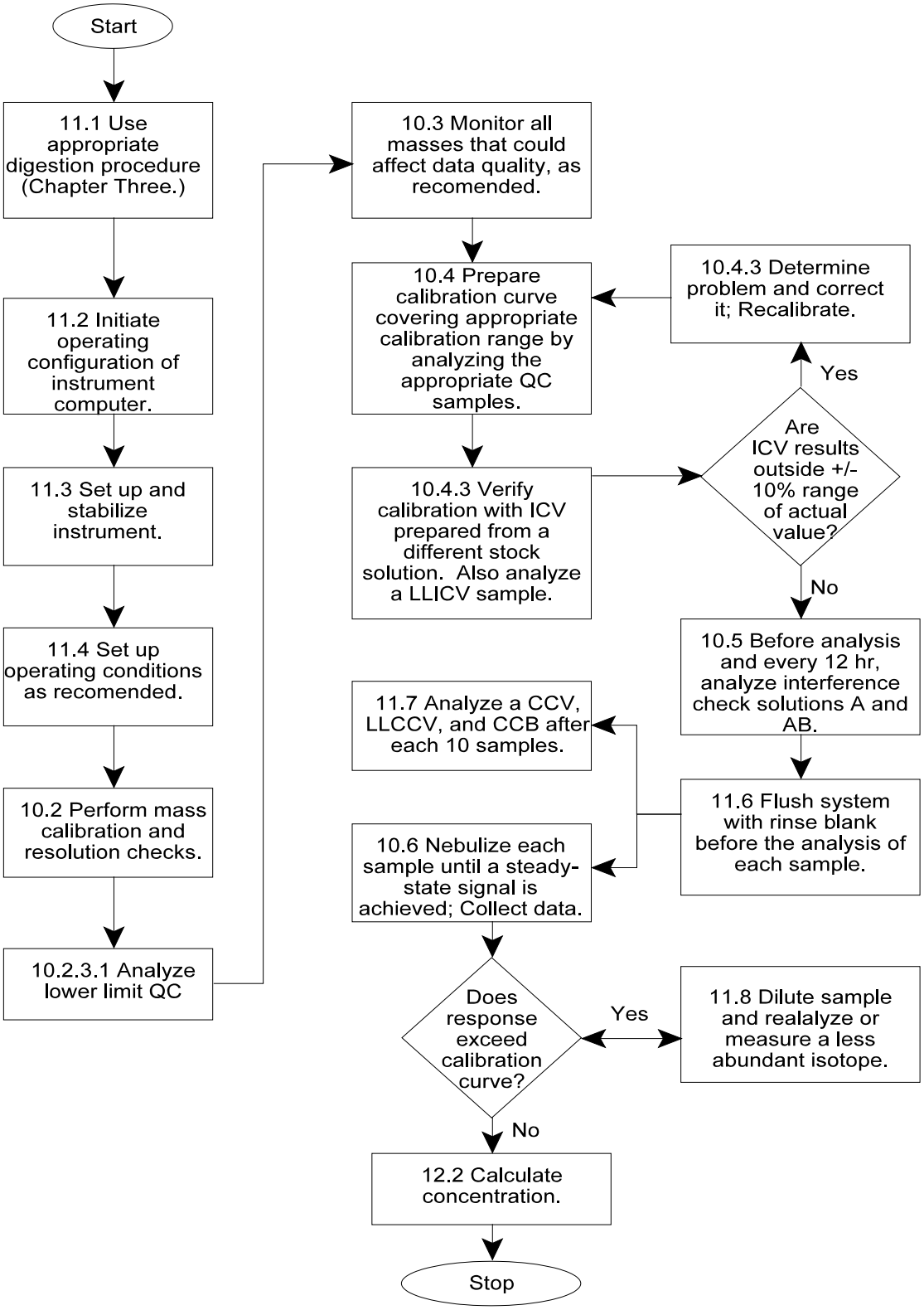
TABLE 7

COMPARISON OF TOTAL MERCURY RESULTS IN HEAVILY CONTAMINATED SOILS

Soil Sample	Mercury in µg/g	
	ICP-MS	CVAA
1	27.8	29.2
2	442	376
3	64.7	58.2
4	339	589
5	281	454
6	23.8	21.4
7	217	183
8	157	129
9	1670	1360
10	73.5	64.8
11	2090	1830
12	96.4	85.8
13	1080	1190
14	294	258
15	3300	2850
16	301	281
17	2130	2020
18	247	226
19	2630	2080

Source: Ref. 16.
These data are provided for guidance purposes only.

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



Appendix H

LacCore: National Lacustrine Core Facility / Limnological Research Center Laboratory (LacCore/LRC) Standard Operating Procedures

Total Inorganic Carbon (TIC, Carbonate) Coulometry

Total Inorganic Carbon coulometry (TIC) measures the amount of inorganic carbon contained in lake sediments or water samples. The TIC content of sediments can be related to a number of factors such as rates precipitation of carbonate minerals or introduction of detrital carbonates into the system. The LRC CO_2 Coulometer can be used to rapidly determine TIC from either water or sediment samples.

Principles

Carbon dioxide gas evolved by dissolution in acid from carbonates in the sample is swept by a gas stream into a coulometer cell. The coulometer cell is filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. Carbon dioxide is quantitatively absorbed by the solution and reacts with the ethanolamine to form a strong, titratable acid which causes the indicator color to fade. The titration current automatically turns on and electrically generates base to return the solution to its original color (blue).

Equipment and Procedure

To measure TIC, carbon contained within carbonate minerals such as calcite, dolomite, siderite, etc., we use a UIC model 5030 Carbonate Carbon apparatus. Five mL of acid (we prefer HCl) serves to evolve CO2 from the sample which is swept into the Carbon Coulometer where it is detected and displayed on a digital screen in terms of micrograms (or any other operator-selectable units) of carbon.

Cell Preparation

The coulometer cell is typically left set up (a change from the older procedure), so unless you are getting bad numbers, you should rarely have to clean or refill the cell.

Note: you must wear appropriate gloves when handling coulometry solutions. A pair of butyl rubber gloves hangs in the cabinet with the columetry solutions. For the rest of this procedure, you must wear regular lab gloves to protect your hands from the acid. Cell filling and cleaning must be done in a fume hood.

1. Fill the main chamber of the coulometer cell with 50-75 mL of cathode solution (large plastic bottle).

2. Place the magnetic stir bar in the bottom of the cell body and insert the cell top with the coiled platinum electrode into the cell. The electrode should be opposite the fritted arm.

3. Add 0.25 cm (enough to cover the bottom) potassium iodide (KI) to the bottom of the side arm (anode compartment) of the cell.

4. Fill the side arm with 10 or more mL of anode solution so as to cover the filter and submerge at least 0.5 cm of the silver anode in solution; the amount of liquid will vary as the anode is consumed (over a period of months) in the analysis.

5. Place the solid silver electrode into the side arm with the silver submerged in the solution.

6. Make sure the glass of the cell is clean and free of grease, fingerprints, water spots, etc., which affect transparency (and thus %T). Wipe/polish with a paper towel or Kim-Wipe, or wash if necessary.

7. Place the assembled cell into the coulometer cell holder. The side arm should extend out the front and against the right wall of the holder, with the platinum electrode and gas inlet tube toward the back of the holder, *out of the light path*.

Set Analysis Parameters. Check these parameters but most should be already set.

8. Rotate the MODE selection thumb wheel to the 1 position which gives the display of units of micrograms (µg) of carbon to 0.1 units.

9. Rotate the TIME SET thumb wheel until the desired analysis time is displayed (generally 4-7 minutes for TIC).

10. Set the RUN/LATCH switch to the RUN position for continuous analysis. LATCH freezes the display at the time set.

11. Set the COUNTS/TIME switch to COUNTS position so that you can watch the counts of carbon on the display.

Operation

12. Make sure coulometer cell current is OFF.

13. Turn ON the main power switch.

14. Set air flow for internal and adjust to 75-100 cc/min.

15. Connect the cell to the cell to the Carbonate Carbon Apparatus using a one-way (check) valve. Only inset the gas tube in the cell when air is flowing, to avoid coulometer cell solution being siphoned back into the KI scrubber.

16. Attach the electrodes to the cell outlet terminals - red to red, black to black.

17. Turn ON coulometer cell current.

18. Allow cell current to titrate the cell solution to its endpoint (solution color becomes blue with %T at 29. If it is lower than 29%, check that the light path is unobstructed and adjust the arrangement of the tube and electrode to correct).

19. (Heater control is broken - do not use.)

You are now ready to begin the analysis.

Analysis Procedure

1. Run a blank sample using an empty sample container. The blank is normally less than 10 µg C in five minutes.

2. Follow the blank by one or more standards (standard $CaCO_3$ is found in a desiccator near the balance). For best precision, material for each analysis should contain 1-3 mg of C. For our standard calcite, this means that you should use about 10-20 mg of standard.

3. Weigh a sample or standard into a clean, dry, tared test tube and attach to apparatus. Sample should contain 1-3 mg of C; adjust the quantity as you begin to see how much carbon tends to be in your samples. Record sample weight in spreadsheet.

4. Pump 5 mL of acid into the reaction tube. RESET the coulometer.

5. When all of the CO_2 is evolved and titrated, (recognized by a stable coulometer display and a %T of 29), record the value in the spreadsheet.

6. Remove the sample tube, pour residue into a waste container, begin next analysis. Wash tubes and rinse in DI water; let dry completely (can use 100 C oven) before reusing.

7. Neutralize the waste acid with soda ash as you go.

8. Run one standard and one duplicate analysis every ten samples (or more if desired).

Calculations

There is a spreadsheet to calculate %TIC (ccoul.xls on the desktop). The calculation is as follows:

%TIC = {(µg C[display value] - per minute µg C[blank value]) / µg sample weight} x 100

Note: the formula subtracts the per minute blank value (blank value/minutes of counting).

For pure calcium carbonate the value should should be 12.00%. (We accept values from 11.75%-12.25%.) Other carbonates will have varying carbon percentages according to the table below.

Mineral	Cation(s)	C	O_3	mw	%C
$CaCO_3$	40.08	12.01	48.00	100.09	12.00%
$MgCO_3$	24.31	12.01	48.00	84.32	14.24%
$(Ca,Mg)CO_3$	64.39	12.01	48.00	184.41	13.03%
$FeCO_3$	55.85	12.01	48.00	115.86	10.37%
$ZnCO_3$	65.38	12.01	48.00	125.39	9.58%
$MnCO_3$	54.94	12.01	48.00	114.95	10.45%

Shut-down (Carbonate Carbon Apparatus)

The Carbonate Carbon Apparatus should be shut down during periods of non-use.

Remove the tube from the cell.
Turn off main power switch.

Note: To prevent residual acid from marring the exterior of the apparatus, keep a sample tube connected to the apparatus when the system is not in use.

Shut-down (Coulometer)

Short periods (during the day)

Before turning off air flow, disconnect inlet gas flow line into the colometer cell. This prevents coulometer solution from being siphoned out of the cell.

Overnight or longer

Turn OFF the cell current and main power supply.

Cell Changing and Clean-up

Note: Solutions should also be replaced when over 100 mg of carbon have been titrated (for 100 mL of cathode solution).

Turn OFF cell current and main power supply.

Unplug electrodes and remove cell from holder. Replace jumper strap between cell current terminals to protect them.

Dispose of the main chamber solution (cathode solution) into the cathode waste solution bottle. Be sure to remove the stir bar first or be prepared to retrieve it from the waste bottle with a magnetic stir bar retriever. Start a new waste bottle (and label correctly) if necessary.

Dispose of the side arm solution (anode solution) and residual KI into the anode waste solution bottle. Start a new waste bottle (and label correctly) if necessary.

Rinse both cell body and the electrodes thoroughly with DI water.

Clean the glass frit in the anode compartment by pulling acetone through the frit with a vacuum.

Rinse and dry all components.

Store cleaned cell in cell holder and return other components to the drawer.

Periodic Mainetenance and Scrubber Changing

Changing Scrubbers

Air Scrubber (40% KOH)

The KOH solution removes CO_2 from the carrier gas, and should be changed once every week during regular use or when the solution becomes thick and foamy. If a fresh KOH solution is foamy, it should be diluted with DI water.

Preparation

Weigh out 40-45 g of KOH and dilute to 100 mL with DI water. Note: Use caution when adding water to KOH as the reaction is exothermic.

Filling

Remove the dispersion tube, bushing and O-ring from the air scrubber assembly.
Place 15-20 mL of KOH solution in the body of the air scrubber.
Replace the dispersion tube, O-ring and bushing. Slide the dispersion tube through the bushing and O-ring so the fritted end is near the bottom of the scrubber.
Hand-tighten the bushing/O-ring seal and place the filled scrubber in its clamp.

Sample Scrubber (50% KI, pH=3)

Preparation

Weight out 50g of KI and dilute to 100 mL with DI water.
Use H2SO4 to acidify to approximately pH = 3.
Fill the fritted sample scrubber with 10-15 mL of the scrubbing solution.
Acid Solution

One can use a variety of acids to react with the carbonates. Originally we used a 2N HClO4 solution but have since switched to using 2N HCl. The procedure for mixing these solutions is given below.

2N HClO4 Dilute 109 mL of 9.2 N HClO4 in 391 mL of DI water.
2N HCl Dilute 172 mL of 37% HCl in 328 mL of DI water

Note: Always add the acid to the water, not the water to the acid.

Loss-on-Ignition

Purpose
Water, organic matter, carbonate mineral, and siliciclastic+diatom content are estimated by sequentially measuring weight loss in sediment core subsamples after heating at selected temperatures.

A compositional profile can be generated rapidly and for very low cost. This profile is sufficient to develop a general sense of core stratigraphy and often is sufficient for correlation between cores.

The results are accurate to 1-2% for organic matter and carbonate in sediment with over 10% organic matter. In clay- or diatom-rich sediment, water of hydration is lost during the carbonate burn, resulting in errors of up to 5% for carbonate analyses (and "false positive" carbonate content in carbonate-free sediments). If high precision (0.1%) is needed, or if sediment is in short supply, coulometric analysis is recommended.

A nonprogrammable Lab Line L-C oven is used for the 100ºC drying step. Other drying ovens are also available in the lab. A drying oven rather than a furnace is used for the 100°C step because the furnaces ramp up to temperature quickly and may overshoot 100°C by an amount that could affect the analysis.

A Fisher Scientific Isotemp programmable muffle furnace is used for the 550°C and 1000°C steps. This is a multiple mode instrument capable of reaching 1125°C and controlling temperatures to better than ± 15ºC with a ± 10ºC temperature uniformity. The programmable circuit will provide the necessary corrections to maintain temperatures at established set point. This furnace holds 200 samples at a time. Another furnace, the Lindberg Blue M, is available for use as a backup, but only holds 50 samples. This is a 2 mode instrument capable of controlling temperatures to better than ± 10ºC. The automatic reset circuit will provide the necessary corrections to maintain temperatures at established set point.

Procedure Summary
Subsamples are placed in weighed crucibles and weighed. Weight loss is measured after heating at 100ºC overnight to remove water, at 550ºC for four hours to remove organic matter, and at 1000ºC for two hours to remove carbonates. After each heating step, the firebrick holding crucibles is allowed to cool completely in the oven or furnace before weighing, or placed in a desiccator if crucibles cannot be weighed immediately. Samples must be cool so that convection currents do not affect the balance, and kept in the oven, furnace, or desiccator so that they do not absorb atmospheric water. Samples must not be placed in a non-venting desiccator when warm.

Ash left at the end of the procedure can be saved for analysis of remaining elements as oxides.

Only one heating step can be accomplished each day, because the 100°C drying time, and the ramp-up and cool-down times of the furnaces are all >8-10 hours. The user should thus plan five days, ideally consecutively:
Day 1 Weigh crucibles (if necessary), subsample, and weigh (initial or wet weightt); place samples in drying oven at *100°C* (allow several hours for these steps, depending on subsampling complexity).
Day 2 Turn off oven, let samples cool, weigh (100°C, dry weight, or water loss); place samples in furnace at *550°C for 4 hr* (about 0.5-1 hour per tray of 25 samples).
Day 3 Weigh (550°C or organic matter loss); place samples in furnace at *1000°C for 2 hr* (about 0.5-1 hour per tray of 25 samples).
Day 4 Weigh (1000°C or carbonate loss), discard or save sample residues, wash crucibles, place crucibles back in trays, place trays of crucibles in furnace at 1000°C for 2 hours to completely clean the crucibles.

Day 5 Turn off oven, allow crucibles to cool completely, remove trays from drying oven, cover with foil, and place in desiccator for reuse (1-2 hr). Label these trays as clean and ready to be reused.

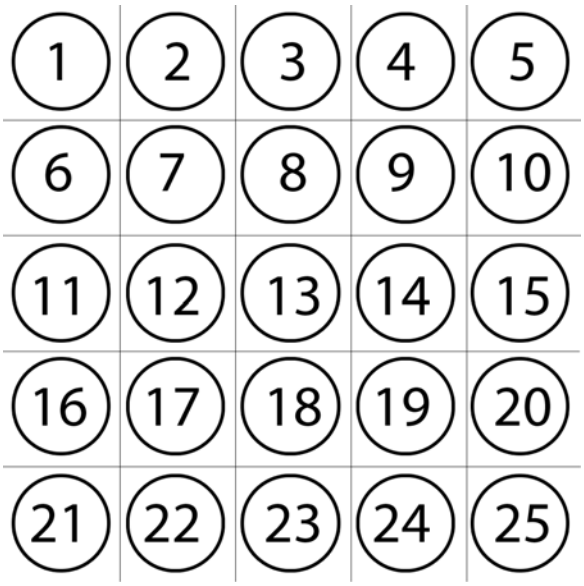
Equipment
Ceramic crucibles
Firebricks drilled to accept crucibles
Sampling device (spatula, syringe)
Desiccator(s)
Drying oven
Muffle furnace capable of reaching 1000°C
Balance weighing in grams to 4 decimal places

Safety
The most obvious hazard in LOI is being burned by hot samples fresh out of the furnace. Be patient. The high-temp gloves and mitts are only good to about 350°C and can be awkward to use.

The muffle furnaces each have a thermocouple (looks like a white stick with metal protruding from the end) which penetrates in through the back of the chamber. It is easily damaged, so be careful not to bump it when adding or removing samples.

Procedure Detail
1. Select and weigh 25 crucibles per fire brick tray. You can prepare up to 200 samples (eight trays) for analysis at a time.
    a. Never touch crucibles with your hands. Skin oils will add weight and introduce error to your results. Always use a pair of tweezers when handling crucibles.
    b. The crucibles are numbered with permanent glaze. Check to see that they are in order in the brick (see below) and that you are starting with the lowest numbered crucible in your tray. Keep good notes! As soon as you've mixed things up the data are useless.
    c. When not burning or being weighed, the crucibles and the samples they contain must be stored in a desiccator. Make sure there is enough desiccator space for the number of samples you hope to analyze. Wait until the samples are cool (<30°C) before putting them in the desiccator: the decrease in pressure upon cooling of the air in the desiccator will vacuum-seal the desiccator shut and it'll be very difficult to open.
    d. Always remove aluminum foil before placing trays in drying oven or furnace
2. Record your crucible weights in the LOI template spreadsheet [*saved in transfers/SOPs/ as* **LOI.Template.xls**]. This new template will highlight (in red) any weights entered that are clearly incorrect (i.e., less than or equal to the empty crucible weight or greater than or equal to the weight of the preceding burn).
3. Place some sample (~1-5 cc) in each crucible and weigh. Weighing should be done as soon as each tray is filled, do not wait to fill multiple trays before weighing. This is your *wet weight*. Record in LOI spreadsheet. *Note:* if you use the **LOI macro** (more about which later), the samples do not have to be volumetric.
4. Heat these samples at **100-105°C overnight or for at least 12 hours in** the drying oven. This will evaporate water and the resulting weight will be your *100°C weight*. Let samples cool in the oven, until <30°C, before weighing. If you cannot weigh the samples immediately after they cool, place in a desiccator with aluminum foil between each tray until you can weigh them.

5. After weighing and recording your *100°C weight*, return the samples to the furnace for a **4-hour burn at 550°C**. This will burn off organic matter. The following day, after samples have cooled in the furnace, samples can be weighed. If you cannot weigh the samples immediately after they cool, place in a desiccator with aluminum foil between each tray until you can weigh them. This will allow samples to take in air moisture and throw off your weights. See furnace directions below.
6. Record your post-550 burn weights in the spreadsheet and return the samples to the oven for a **2-hour 1000°C** burn. This will burn off a combination of carbonate material and some of the water stored in the lattice of clay minerals and diatom silica. See furnace directions below.
7. After cooling, record this weight as your final measurement. You may discard the sample remaining in the crucible, or save it for another analysis.
8. Run the LOI Macro. See directions below.
9. Clean the crucibles for the next user.
    a. Two buckets are needed and should be in or near the sink in room 680A. Fill one bucket with warm tap water and add soap from the bottle labeled "Lab Soap" above the sink. Fill the other bucket with low-purity deionized water from carboy above the adjacent sink.
    b. Remove any remaining residue and place the crucibles in the warm tap-water bath.
    c. Using a brush found above the sink, scrub the crucibles until all baked on residue is gone. Some discoloration will remain.
    d. Rinse the crucibles in the DI water bath, shake dry and place in the firebrick tray following the numbering system designated in the figure on the right.



    e. Place all washed trays of crucibles in the furnace and burn at 1000°C for two hours (in the same manner as the carbonate burn).
    f. The following day, remove all trays from the furnace, cover with aluminum foil and place in appropriate desiccators. Use the "Cleaned 1000°C" crucible icons or label the trays "Cleaned and burned at 1000°C" between each tray so that the next person knows they are ready to be used.

How to use the Lab Line L-C oven

1. Open the oven and place your trays on the shelving in the oven. Load in the top trays first to prevent contamination of the samples. Close the oven door
2. Turn on the oven using the switch on the front panel.
3. Set the temperature knob about ¾ of the way between a setting of 4 and 5 to heat the oven to 100°C.
4. The oven does not have a temperature feedback control system, it is a good idea to periodically check the temperature on the oven to make sure it reaches 100°C but does not greatly exceed 100°C.

How to use the Isotemp muffle furnace in Ramp and Soak mode

1. Open the flue on top of the furnace.
2. Turn on the Furnace using the switch on the front control panel.
3. Open the furnace and place your trays on the shelving in the furnace. Load in the top trays first to prevent contamination of the samples. The muffle furnace has a thermocouple (looks like a white stick with metal

protruding from the end) which sticks in through the back of the chamber. It is easily damaged, so be careful when adding or removing samples not to bump it. Close the furnace door.

4. Verify that the Run LED is not on. If it is on, press Run until the light goes out.
5. Press the following sequence of buttons in the left most column.

Button	Top Display	Lower Display	Description
Menu	No	program	Furnace is not in program mode.
UP	Yes	program	Select yes to set program parameters
Menu	1	step	The first step in the program
Menu	SP (Set Point)	styp (step type)	is a set point.
Menu	(550 or 1000)°C	sp	This is the temp from the last time the program ran.
Up/Down	(550 or 1000)°C	sp	Use the up or down keys to set to 550 or 1000°C.
Menu	20° C	rate	The ramp up rate should always be 20°C for LOI.
Menu	No	retn (return)	No return for this step,
Menu	2	step	move on to step two in the program,
Menu	Soak	styp	a soak step.
Menu	(4 or 2)	hour	This is the length from the last time the program ran
Up/Down	(4 or 2)	hour	Use the up or down keys to set to 2 or 4 hours,
Menu	0	min	0 minutes,
Menu	0	sec	0 seconds,
Menu	No	retn	No return for this step.
Menu	3	step	Move on to step three in the program,
Menu	end	styp	to end the program,
Menu	off	end	by letting the furnace cool to room temp.
Menu	yes	save	Save the program.
Menu	actual temp	set temp	You have exited the program parameters.

6. Press run twice to run the program, the run light should be solid (not flashing) and the program will automatically start to ramp up to temperature. You can see the set temperature and the actual temperature on the display.
7. Once the furnace has cooled down, you can close the flue and turn off the furnace. If the alarm LED is lit up on the control panel please notify staff, this means that the actual furnace temperature exceeded the set temperature by more than 25°C
8. Remove the bottom shelf of samples first, to prevent contamination.

How to use the LOI Macro

To use the macro [*saved in transfers/SOPs/LOI as* **LOI.Macro.xls**], the spreadsheet that contains your LOI data must be in the following format (column titles):

Depth, Crucible Weight, Wet Weight, Weight (100°C), Weight (550°C), Weight (1000°C)
or
Depth (Top), Depth (Bottom), Crucible Weight, Wet Weight, Weight (100°C), Weight (550°C), Weight (1000°C).

These columns and the data within them are the ONLY cells that may be filled in on the page, or the macro will malfunction. If you have supplementary data such as crucible number, core names, notes to self, etc., cut them from this spreadsheet and put them in another sheet in the same workbook.

Save the data spreadsheet as a **new file** (the macro overwrites the opened file) and close it. Open up the **LOI.Macro.xls** file. (Click “enable macros” in the warning window that pops up.) Go to Tools--> Macro--> Macros (or press Alt-F8). The "macro name" line should read "A1" and be highlighted. The first line of the section below A1 should read "LOI." Click "Run."

The next box that pops up asks for the file name (as saved on the spreadsheet), some info about the coring site (nonessential), whether your depth intervals are single or you've used two columns for top and base depths (determined by which format for column titles you used above), and whether you did a $CaCO_3$ (1000°C) burn. Once you've filled in and selected the appropriate options, click "OK" and the macro will perform its magic. It will probably not find your file at first, but you have the option of browsing for it.

The resulting data will be placed in columns to the right of your original data.

*For a comprehensive review of best practices and comparative LOI methods, please see Heiri et al, Journal of Paleolimnology 25, p. 101-110.

STANDARD OPERATING PROCEDURE: TOTAL CARBON/TOTAL NITROGEN (TC/TN)

Preparation and analysis of MN lake sediments submitted to the LLO for TC/TN analysis

Sample condition –

Samples were received from the LRC freeze-dried and ground (Myrbo) in snap-top plastic containers. Some samples contained visible vegetative material. Some samples contained small pebble sized material. Inhomogeneity may result in greater analytical variability or misleading results.

Preparation –

Samples were mixed with a metal spatula before subsampling. Milligram quantities of sample were packed into tin capsules and weighed on a microbalance. Sample FS-63 Caribou was not stable weight-wise. The entire sample was placed in a 60°C oven for 3 hours and cooled in a desiccator before subsampling.

Instrumentation, Analysis and Quality Assurance –

Acetanilide was used as a calibration standard and as a quality assurance sample. A MN Lake Sediment sample prepared in duplicate and a QA sample were run at least every tenth sample. All QA samples were within ±5% of the known Carbon/Nitrogen weight percent for that material.

Elemental analysis was performed using a Costech 4010 ECS.

Paraphrasing from Costech literature: At the start of an analytical cycle, helium carrier gas was switched to a volume of oxygen. Samples were dropped sequentially into a combustion reactor at 1020°C prior to the arrival of oxygen. The sample and tin capsule reacted with oxygen and combusted at 1700-1800°C. The sample was broken down into elemental components, N_2, CO_2, and H_2O. High performance copper wires at 700°C absorbed excess oxygen not used for sample combustion. The gases flowed through a water trap and then through a gas chromatography (GC) separation column at 35°C. As the gases passed through the GC column, they were separated and detected sequentially by a thermal conductivity detector (TCD). The TCD generated a signal proportional to the amount of element in the sample. Costech EAS software compared the elemental peak to a known standard material (after calibration) and generated a report for each element on a weight basis.

Each sample chromatogram was visually inspected. Manual integration was performed as necessary to use only the area of the element of interest in calculations.

Results were manually transferred to the spreadsheet provided by Amy Myrbo and reported via email.

Appendix I

LacCore Field Survey Sampling Procedures by Dr. Myrbo's Research Group - Standard Operating Procedures

WILD RICE SULFATE STANDARD FIELD SURVEYS 2011 & 2012:

FINAL REPORT

Amy Myrbo

University of Minnesota

Submitted May 21, 2013

Abbreviations

AVS – acid volatile sulfide
DNR – Minnesota Department of Natural Resources
LacCore – National Lacustrine Core Facility of the University of Minnesota
LLO – Large Lakes Observatory of the University of Minnesota-Duluth
LRC – Limnological Research Center of the University of Minnesota-Twin Cities
MDHL – Minnesota Department of Health Laboratory
MDL – method detection limit
MPCA – Minnesota Pollution Control Agency
PI – principal investigator
QAQC – Quality Assurance/Quality Control
RL – reporting limit
SCWRS – St. Croix Watershed Research Station of the Science Museum of Minnesota
SO_4 – sulfate
UMN – University of Minnesota

Contents

Introduction

Overview of the 2011 and 2012 Field Surveys

Under contract from the Minnesota Pollution Control Agency (MPCA), the University of Minnesota (UMN) conducted a survey of water bodies across Minnesota in the summers of 2011 and 2012, to assist the evaluation of the State's sulfate water-quality standard to protect wild rice waters (also known as the "wild rice sulfate standard"). This activity, henceforth referred to as the "survey" (or "2011 survey" and "2012 survey") is intended to provide (1) information to the MPCA about correlations between wild rice presence and environmental parameters, and (2) data to be used in development of other phases for the study, including composition of a medium for experimental hydroponic wild rice growth and composition of sediments for experimental wild rice growth in containers (known as mesocosms or microcosms). The 2011 survey was a preliminary effort to collect initial data on wild rice stands and to develop the methods for a larger field survey in 2012.

Team Structure, Management, and Duties

Lead personnel of this ongoing project are: Principal Investigator Dr. Amy Myrbo, Research Associate, LacCore and Limnological Research Center (LRC), Department of Earth Sciences, UMN; Dr. Daniel Engstrom, Director, St. Croix Watershed Research Station (SCWRS); and Dr. Nathan Johnson, Assistant Professor, Department of Civil Engineering, UMN-Duluth. This team works closely with Dr. John Pastor, Professor, Department of Biology, UMN-Duluth. Field technicians for the surveys are drawn from the staff of LRC/LacCore. Laboratory technicians are employees of LRC/LacCore, SCWRS, the Department of Civil Engineering, or the Large Lakes Observatory (LLO), UMN-Duluth, as appropriate for the lab at which analyses were conducted. The Minnesota Department of Health Laboratory (MDHL) conducted analyses of some samples collected in 2012. The research team developed and conducted the survey in close contact with MPCA personnel.

The 2012 Field Survey

The 2011 field survey was described in a previous report to the MPCA (Myrbo 2012). Except where noted, methods remained the same for the 2012 survey.

Duration of the 2012 Field Survey

The 2012 Field Survey began with on-site training of the field crew with MPCA personnel on July 3, 2012. Six field technicians and two lab staff (the PI and the logistics supporter) were trained in boat operation, sampling and sample processing methods, QAQC (quality assurance/quality control) procedures, chain of custody forms, and identification of the wild rice plant. The field survey itself began July 22 and ended September 21, 2012. When the survey was terminated, wild rice plants were beginning to senesce, air and water temperatures were cooling, and the waterfowl hunting season was about to start.

Site Selection

The goal of the 2012 survey was to sample 100 sites. Myrbo worked with MPCA staff to select potential sample sites within lakes, rivers, wetlands, and cultivated wild rice paddies using information provided by stakeholders, and data on the chemistry and distribution of wild rice waters and other shallow water bodies. Figure 1 shows the locations of approximately 1300 wild rice sites identified by the Minnesota Department of Natural Resources (DNR) in its report *Natural Wild Rice in Minnesota* (2008), along with contours of surface water sulfate (SO_4) concentrations based on data in the DNR database.

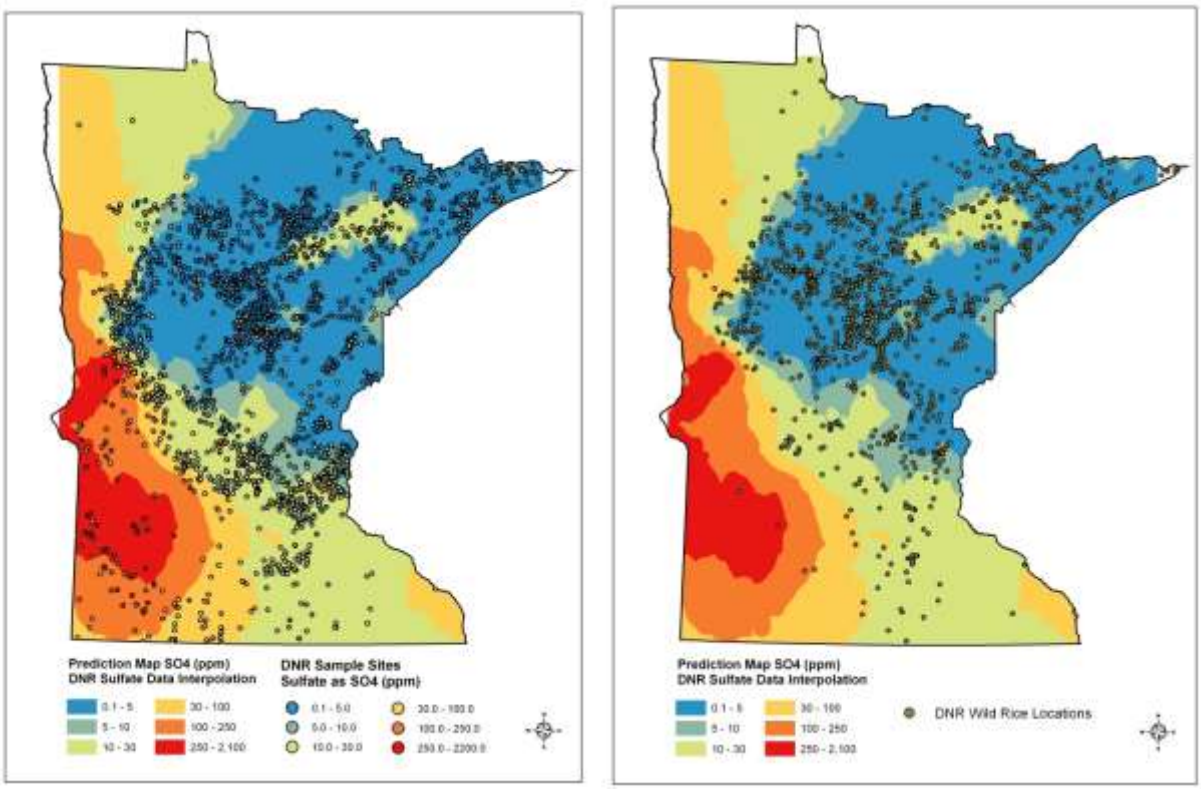


Figure 1. Dissolved sulfate (SO_4) concentrations measured in surface water (left) and distribution of identified wild rice water bodies (right), overlain on interpolated contours of surface water sulfate. Datasets from DNR. Figures prepared by Shawn Nelson, MPCA.

For statistical purposes of investigating the purported relationship between sulfate and wild rice growth, the team sought sites with a range of values in both parameters (i.e., low-sulfate/low-rice, low-sulfate/high-rice, high-sulfate/low-rice, and high-sulfate/high-rice). The team also strove to sample widely across the state, and to sample sites that had a history of past or present drainage of waters high in sulfate into wild rice waters. The MPCA gained permission for the field teams to sample some wild rice waters of the Red Lake, White Earth, and Fond du Lac Reservations accompanied by Tribal resource management personnel; additional permissions allowed sampling in wildlife management areas, State parks, cultivated rice paddies, and access across private land. The sites sampled in the 2011 survey were selected from a large list of waters for which there were historical reports of wild rice growth. In contrast to site selection in the 2011 survey, the 2012

survey included sites without a known history of wild rice presence. Figure 2 presents the sites sampled in the 2011 and 2012 surveys. Appendix D provides details of the sites sampled in the 2011 and 2012 surveys.

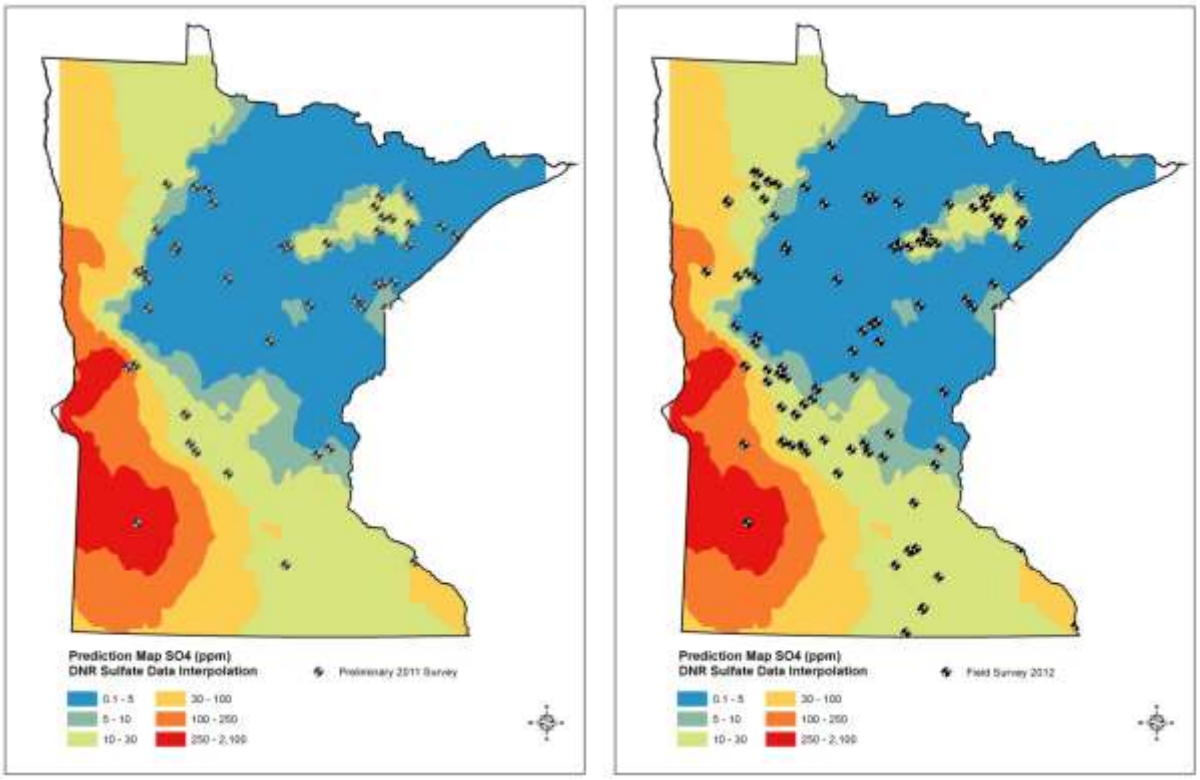


Figure 2. Locations of sites sampled in the field surveys: 2011 survey (left), 2012 survey (right), overlain on surface water sulfate contours as in Figure 1. Figures prepared by Shawn Nelson, MPCA.

Field Campaign

Field protocols were developed in collaboration with MPCA staff. The field sampling protocol is included as Appendix A. The data sheet completed by field crews for each site is provided in Appendix B. In 2012 field crews sampled 112 unique sites (i.e., locations in water bodies) during the survey (see Fig. 2). The complete field and currently available analytical datasets are presented in Appendix D, along with the associated 2011 data. LacCore developed a relational database for this project as part of its existing database system. All data, after being quality checked, are entered into this database.

A team of two persons sampled each site. Two teams were typically deployed at any time. From a canoe or motorboat, depending on access conditions, the team sampled surface water and collected seven or eight short (~50 cm) core samples around the boat. Water and sediment were collected at the same site, unlike in the 2011 survey where water was collected in open water and cores were collected in a wild rice bed. Also in contrast to the methods of the 2011 survey, field crews were

instructed to collect cores at all sites, not only those with wild rice present. In the absence of wild rice, field crews were instructed to collect cores at a site selected using a schema developed by the MPCA and included at the end of the field protocol (Appendix A). At the sampling site the team also conducted a plant survey using 1 m diameter rings placed at four locations around the boat. Plant taxa present were identified, and the percent coverage and number of stems of wild rice were recorded. Plant voucher specimens were collected in some cases. Each 2012 sampling site was assigned a unique "LacCore ID" number beginning with "FS-" for "field survey 2012." In 2011 samples were assigned LacCore IDs beginning with "P-" for "preliminary field survey 2011."

Water and core samples were returned to shore and processed as described in Appendix A. Individual cores were sampled for porewater using 10 cm long Rhizon™ samplers with 0.2 μm nominal pore size (Shotbolt 2010), inserted vertically into the core tops after overlying water was extruded, drawing into evacuated (and pre-treated where appropriate) serum vials. Three other cores at each site were extruded to remove overlying water, then further extruded to a depth of 10 cm below the sediment-water interface, placed in a bowl together under a nitrogen atmosphere, and composited by vigorous stirring. A subsample of this composite sediment was immediately frozen on dry ice for acid volatile sulfide (AVS) analysis and the remainder was refrigerated for later analysis. A nitrogen atmosphere was not employed in 2011. In 2012 the sample for AVS analysis was preserved with zinc acetate prior to freezing.

Field data were recorded on paper copies of the field data sheet similar to that provided in Appendix B. Field technicians entered data into the LacCore database in the evenings as possible given internet connectivity. Data were quality-checked by a different field technician at LacCore. At the end of each day, each field crew sent an email reporting on the day's activities, providing observations on the site(s) sampled and reporting any equipment problems. Site information from these emails is included in the database.

Laboratory Analyses

Sample Handling and Analyses

Water samples were kept frozen or refrigerated, as appropriate, and were transferred to MDHL within seven days of collection. Sediment samples were kept refrigerated and returned to LacCore, where they were thoroughly homogenized, subsampled, and treated as shown in Appendix C. Some subsamples were transferred to SCWRS or the LLO, and the remainder were analyzed at LacCore. Summary statistics for completed analyses, including field measurements, are presented in Table 1.

Remaining Tasks and Timeline for Completion

As of mid-May 2013, the MPCA has not yet finalized the preliminary water chemistry data from the MDHL for the 2012 field survey. In addition, some sediment analyses remain to be completed or finalized (anticipated date of completion follows each analysis in parentheses):

- Phytolith analysis (July 30, 2013) (LacCore)

- Organic grain size analysis (May 30, 2013) (LacCore; completed but not finalized)
- Total phosphorus (TP) (May 24, 2013), phosphorus fractions (June 30, 2013), extractable metals (June 30, 2013) (SCWRS)

LacCore and the associated laboratories are in the process of establishing method detection limits (MDLs) and reporting limits (RLs) for certain analytical methods; therefore, as of mid-May 2013, some low values remain in the database and in the table of summary statistics that will be eliminated (i.e., replaced with a statement to the effect that they are below the RL) when RLs are established.

Certain quantities, specifically alkalinity, charge balance, and ionic strength, will be calculated by the LacCore database but are not complete at this time.

Field sampling sites have been established in the EquIS database by MPCA staff in collaboration with LacCore, and datasets are being uploaded to that database after they undergo QAQC.

Table 1. Summary statistics for 2012 data.

	unit	Average	Minimum	Median	Maximum	5th Pct	25th Pct	50th Pct	75th Pct	95th Pct
surface water pH		7.97	4.01	7.84	9.76	6.79	7.37	7.84	8.66	9.38
surface water spC	uS/cm	328.1	49.9	300.5	1136.0	107.1	233.8	300.5	363.0	565.4
surface water T	°C	23.06	11.30	23.45	32.90	14.90	20.28	23.45	26.43	30.61
Pore water pH		6.82	5.41	6.76	8.07	6.08	6.53	6.76	7.15	7.78
LOI water content	%	72.6	14.7	81.1	95.4	28.5	62.6	81.1	89.3	93.1
LOI organic	%	26.4	1.1	21.9	81.1	2.0	9.3	21.9	42.5	59.9
LOI carbonate	%	12.9	0.7	6.7	74.1	1.9	4.4	6.7	13.4	44.2
LOI inorganic	%	60.5	14.7	61.2	98.1	25.3	39.5	61.2	83.7	94.8
Total C	%	14.96	0.36	14.21	44.21	1.37	4.70	14.21	22.70	32.37
Total inorganic C	%	1.56	0.00	0.67	9.27	0.00	0.02	0.67	2.15	6.25
Total N	%	1.10	0.04	0.99	3.21	0.08	0.30	0.99	1.76	2.52
Total S	%	0.60	0.01	0.35	4.66	0.03	0.15	0.35	0.73	1.74

Appendices

Appendix A. Field protocol SOP

Appendix B. Field data sheet template

Appendix C. Sediment subsampling flowchart

Appendix D. Summary data from the sites sampled in 2011 and 2012

Complete field data can be obtained from the Minnesota Pollution Control Agency.

Appendix E. Standard operating procedures (SOPs)

Loss-on-ignition (LOI)
Total inorganic carbon (TIC) coulometry
Total sulfur (TS) coulometry
Total carbon and total nitrogen elemental analysis (TC/TN)

References

Myrbo, 2012. Wild Rice Sulfate Standard Preliminary Field Survey 2011. Final Report. Submitted to the Minnesota Pollution Control Agency. August 27, 2012.

Minnesota Department of Natural Resources 2008. Natural Wild Rice in Minnesota. A Wild Rice Study document submitted to the Minnesota State Legislature. http://files.dnr.state.mn.us/fish_wildlife/wildlife/shallowlakes/natural-wild-rice-inminnesota. pdf, accessed June 20, 2011.

Shotbolt, L. 2010. Porewater sampling from lake and estuary sediments using Rhizon samplers. *Journal of Paleolimnology*. 44:695-700.

Appendix A

Field protocol for MPCA-SO4 field sampling by LacCore

1.0 Amy Myrbo, 8/14/11
rev. 2.0 Amy Myrbo, 8/28/11 (adjusted protocol to reflect changes made during field trials with MPCA)
rev. 3.0 Amy Myrbo, 9/11/11 (added pore water chemistry sample protocol and blanks/duplicates protocol; removed advice to re-pump serum bottle)
rev. 4.0 Cindy Frickle 7/9/12; Ed swain 7/10/2012; Amy Myrbo 7/10/2012 (adjusted protocol to reflect changes made during field training)
rev. 5.0 Cindy Frickle, 7/12/12 (adjusted protocol to reflect changes made during field crew meeting)
rev. 5.1 Amy Myrbo, 7/19/12 (accepted most changes in document and made penultimate recommendations prior to beginning of 2012 field survey)
Rev 5.2 Ed swain 7/19/12 used pages software on an iPad to add a few suggestions framed by double asterisks: **suggestion**
Rev. 6 7/29/2012 Cindy Frickle made corrections based on first week's sampling
7/29/2012 Amy Myrbo made minor clarifications
8/8/2012 Cindy Frickle made corrections and clarifications based on further feedback in field

⇓ symbol indicates that data should be recorded at this point, or that a note should be made that a sample was taken.

- Review equipment checklists and restock any required equipment.
- Unload canoe/boat and load equipment (when using Kevlar canoe, load only on water). Lash equipment to boat.
- Check for signage about invasive species and check box where appropriate. ⇓
- Check for presence of a water level gauge (sometimes near boat ramps) and record water level if present. Note the location of the gauge. ⇓
- Calibrate Hach meter: Complete calibration log that goes with the meter, noting date, time, calibration, and who completed it. ⇓ Insert pH probe into small, color-coded vial with pH 7.0 solution. Take reading and record as "Before." Calibrate, but do not record the value that appears on the screen. Take another reading and record as "After." Dump used solution into hazardous waste container and re-fill vial from pH 7.0 bottle. Rinse probe with de-ionized water, then repeat process with pH 4.0 solution. Rinse probe again and re-cap in storage solution. Complete process similarly with 1001 µS conductivity solution—using small vial of solution, calibrate to 1001 µS spC. Dump used solution into hazardous waste container. Refill small vial of solution, rinse probe, and re-cap in storage solution. Ensure that calibration log was properly completed, leaving no fields blank. ⇓
- Lock vehicle.

- Proceed to relatively dense wild rice bed (at the same GPS location as a previous crew had sampled the wild rice in this water body, if possible) or, if wild rice cannot be located, choose a site in a water lily bed (either yellow or white). If neither wild rice nor water lilies can be located, use the attached decision tree to decide where to take samples.

- Run boat entirely into thickest part of wild rice bed. Avoid uprooting or otherwise destroying wild rice plants whenever possible. *Caution:* when wild rice seeds are ripe, the elongate part of the seed cover is sharp and barbed, and can pierce the eyeball. Use caution when moving through wild rice beds. Sunglasses and long sleeves are recommended.

- Assess sediment matrix characteristics using soil probe, ⇓ then anchor boat by pushing 2 drive rods into sediment and lashing rods to canoe thwarts. Bottom (female) ends of drive rods that do not have a sediment probe attached must be duct taped over so that sediment does not get stuck up in the rod. Avoid resuspending sediment in the water column by pressing drive rods directly and firmly into sediment surface. Extend outriggers to stabilize canoe.

- Deploy thermal stick and record time. ⇓

- Fill in site info. Record weather and flow conditions. Note which equipment you are using. ⇓

- Record orientation of boat relative to compass rose on data sheet using ball compass. ⇓

- Take site photos: First, photograph lake data sheet, making sure that lake name is visible. Then, in order, photograph toward north, east, south, and west, keeping the boat slightly in the frame at the bottom of each photo. Review photos to ensure that each has acceptable exposure and focus. Delete and re-take any that are unacceptable. ⇓

- Turn on GPS, wait until accuracy is optimal (Garmin 76 should be around ±3m), save waypoint, and then record latitude, longitude, elevation, accuracy, and waypoint number. ⇓

Water and sediment sampling:

- Deploy Hydrolab so that probes are just below water surface on upwind side of boat and collect multiparameter data. Be sure that circulator is on. Record temperature (˚C), specific conductance (spC), and pH. Note spC units. ⇓ Rinse probes with de-ionized water before replacing caps containing storage solution.

- Find Secchi depth on shady side of boat, without wearing sunglasses. Then find water depth in the same location using Secchi disk. ⇓

- Put on nitrile gloves and rinse two master water sample bottles three times with subsurface water, filling on sunny side and dumping on shady side of boat (dumping in same location where Secchi disk was lowered). Hold bottle underwater and fill, being careful not to disturb sediment or collect submerged macrophytes or scum, etc., floating on surface of water. Do not

touch any metals during sampling such as boat parts or sunscreened skin. ⇓ Cap bottles and place in cooler.

- Rinse polycarb tubes. ⇓ Collect 8 cores using tabbed tubes: Retain tension on rope while pushing gravity corer deeper into sediment. Pull corer up and – keeping bottom end of core underwater and holding core upright – insert piston. Cores should be taken 1m apart from each other and from the thermal stick. Always hold cores upright. Avoid any area where sediment may have been disturbed, including area where Secchi disk was lowered. Place cores in core holder and cover with white paper bags.

- Collect core for repository in an undisturbed location. Use polycarb without tabs—hold corer so that piston is **not** pushed all the way up and wrap duct tape around corer and tube to hold in place. After pulling up core, cut down to 5-10 cm above sediment/water interface and top thoroughly with Zorbitrol, cap, tape, label, and measure core sediment length and total core length. ⇓ On core tube, write lake name, site ID (FS - - -), and draw "up" arrow. Place in shade.

- If a core is lost, spilling sediment that might contaminate the next core, record this, move position one boat length, record new position, and continue, taking remainder of cores as specified above. Take care not to core in any spoiled or previously cored location. ⇓

Vegetation sampling:

- Use 1 m diameter hoop to characterize abundances of plant types. Place hoop even with seats on both sides at front and back of boat.

- Estimate rice coverage in each hoop. ⇓ Count rice stems in each ring. ⇓ Note abundance of other plants within hoop area, including specific species (%sp) whenever possible, using plant guide for identification. ⇓ Look under floating leaves; sum can be over 100%. Take a picture of each survey space. ⇓

- Describe the condition of the wild rice plants and general locations of stands. Estimate relative abundances of flowering rice plants and plants with seeds. Note overall abundance of wild rice (vs. open water) in representative rice stands on the lake, or as far as you can see. ⇓

- Collect voucher specimens: Pull out two wild rice plants (with flowers or seeds if possible), rinse sediment from roots, accordion fold and place into zippered plastic bags, noting site name and water depth. Put in cooler. [If rice is not present, collet other species as per decision tree instructions.]

- Remove and rinse thermal stick. Record time. ⇓ Remove drive rods, cleaning off any sediment. Secure all equipment and return to shore.

Shore processing:

- Keep all samples either in the shade (repository core) or in the cooler (all other samples, including plants) at all times.

- Wear gloves for all on-shore processing.

- Pore water sampling: Extrude so that sediment surface is at top of core tube. Set up ring stand with core, in a secure spot in the shade. Place a piece of Saran wrap over the top of the core and poke a small hole in the center. Evacuate serum bottle for 70 mL sample for TP/TN/DOC, first, using a needle and hand pump. Pump to approximately 25 inches Hg internal pressure, then remove needle slowly. Attach needle to Rhizon connection, sealing connection with Teflon tape. Seal any other connections between tubing pieces as well. Insert Rhizon sampler into sediment so that clear connector is just below the sediment surface. Place serum vial upside-down in ring stand clamp. Pierce septum with Rhizon needle, take out most of slack in Rhizon tubing, and tighten clamp rod on vertical rod so that tubing is as straight as possible. Leave to draw until fluid reaches the desired volume of 70 mL (bottle should be marked with approximate 70 mL line). Insert additional Rhizon(s) if sipping becomes slow due to clogging of the porous part. Keep pushing Rhizon in if core surface lowers. When finished sipping, remove the needle from the bottle before removing the Rhizon from the core. Remove needle slowly to avoid air invasion. If that core will not yield 70 mL, consider achieving the 70 mL goal by switching the serum bottle to the spare short core. Make a note on the field sheet if you do so. ⇓

- Meanwhile, set up second, third, and fourth short cores as described above. Evacuate the serum bottle for nitrate/metals, sipping 50 mL of pore water. Follow same procedure for 30 mL sample used for silica/chloride/sulfate. For sulfide bottle, (preloaded with zinc acetate, with nitrogen headspace), place Rhizon end into sediment then stick needle attachment into a evacuated "sacrificial" bottle to draw air out of the sipper. Once you see water pulling through into the bottle, remove needle and stick into sulfide bottle. (NB: Do not re-use needles from sulfide bottle in other bottles as this bottle contains zinc acetate and may contaminate other bottles.) Record start weight of sulfide bottle. ⇓ Sip 50 mL of pore water into sulfide bottle.

- Take practical samples – as much as you can get until it gets slow and oxygen invasion is a concern. Ensure that top of Rhizon is always below the sediment surface, sipping pore water, and not above it, sipping air. **It is particularly important that air is not introduced into the sulfide sample.**

- Compositing cores: (This procedure and those below should be done while sulfide sample is sipping.) Turn on high-purity N_2 gas to fill glove bag. Line bottom of glove bag with a piece of cardboard covered with plastic to make any necessary cleanup easier. Set up extruder. Place first core on extruder and push up piston until all water has been removed (i.e., sediment surface is at top of tube).

- Porewater pH measurement: Using one of the cores that will be composited, insert the pH probe below sediment surface to 5 cm depth marked on probe. (If sand or gravel is present in

core, use spatula to push aside sediment to make a narrow hole for the pH probe, to avoid scratching the electrode.) Hold there until reading stabilizes. Record reading. ⇓

- Place extruder tray on top of tube. Extrude top 10 cm of core, scraping mud into small, clean bowl bucket as necessary, mixing as little as possible. Discard remainder of core. Repeat with other two compositing cores, adding to the same bucket. Place sample into nitrogen glove bag. Seal bag that has been flushing with high-purity N_2 for at least 10 minutes. Record observations of sediment texture, color, odor, etc. Stir composited sample vigorously to homogenize. Using rubber scraper, scoop enough subsample into glass AVS jar to fill approximately half full. Add zinc acetate preservative from vial (equivalent to 1 mL of 1N zinc acetate/50 mL sediment), then mix well to incorporate preservative. Fill headspace with N_2 and close cap. Turn off nitrogen gas. Place AVS jar in cooler with dry ice, but not directly on the dry ice because rapid freezing at the bottom may cause breakage. Isolate the jar from the dry ice with a piece of cardboard.

- Scoop remaining sediment into large jar. ⇓ Place large jar in cooler with ice.

- Water sample splitting: Put on nitrile gloves. Shake bottle. If sample contains particulate matter, let settle prior to splitting and do not shake. Split among the 3 subsample bottles; avoid direct contact between bottles while pouring. Add sulfuric acid to the "Nutrients" bottle, close tightly and invert to distribute acid. Put empty acid vials into a Ziploc bag labeled with a hazardous waste label for disposal. DO NOT add acid to the "Metals" bottle—this will be done in the MDH lab. Tighten all caps *again* to ensure that samples are tightly sealed. Place all samples in cooler. Triple rinse amber sample bottles with deionized water. ⇓

- Hach water color: Fill outer test tube with clear water, either distilled water so that the meniscus is even with the upper line. Fill inner test tube to same level with unshaken water sample. Look through tubes towards sky and turn color wheel until the two tubes' colors match. Record value. If water is too colored (>100), remove mirror and multiply value by 5. If still too colored, leave mirror out and dilute sample by half (empty to lower line and add distilled water to reach the second of the three lines), and then multiply the observed value by 10. Rinse lake sample tube with deionized water. ⇓

- Transparency: Shake second water sample bottle. Fill Secchi t-tube. In the shade, and without sunglasses, lower Secchi disk until it is no longer in view from above. Record depth. ⇓ Bring disk back up until just in view again. Record depth. ⇓ Average these two values and record as t-tube Secchi depth. ⇓

- Review data sheet to ensure that all fields have been entered. Do not leave any spaces blank. Make any necessary field notes. ⇓

- Decontamination: IF SITE HAS BEEN IDENTIFIED AS HAVING INVASIVE SPECIES PRESENT, while at the site, decontaminate all equipment using appropriate method (boiling water, alcohol, abrasion, etc.). At all other locations follow DNR protocol of removing aquatic plants from boat and trailer: rinse, drain, and dry. ⇓

- Complete MDH Chain of Custody form for samples: Using attached model, fill out one form for each site. Record names of both samplers, location ID, sample point, date, time when samples were collected (i.e., from lake, not time of shore subsampling), and lat/long of the site (under Sampler Comments). Sign form. All fields pertaining to Matrix code, quantity of containers/preservatives, and analyses should be already completed on the form. Direct any questions about form to Ed Swain. Place forms in Ziploc bag inside of cooler with samples. ⇓
- Do not take completed field data sheets back out onto boat. Enter data daily into database.
- Upload and name photos in a new folder in Transfers. Folder name should contain Location ID (FS-xxx) and Sample Point (Site Name/DOW#). All files should include the Location ID in their names.

- Press plants within two days of sampling (but preferably the same day of sampling), provided the plants have been kept cool and out of the sun. For each individual plant, arrange it accordion-like across the inside of a folded sheet of newspaper. With a waterproof Sharpie, write on the outside of the newspaper the type of plant (WR for wild rice, unknown for an unknown plant, etc.) location, date the plant was sampled, and your last name. You may put more information on paper with the plant, but the purpose of writing on the top of the newspaper is to be able to sort samples without opening the newspaper. Put the folded newspaper between blotting paper sheets, which are between ventilating cardboard pieces, within the plant press. Compress the stack of plants and allow to dry. Change newspaper daily to avoid mold, especially in the first few days after collection, including weekends after returning from the field.

- Re-freeze cold packs as needed and ensure that there is sufficient dry ice to keep AVS samples frozen.

- Send brief report of day's activities to SO4-project listserv.

End of week:

- Leave all equipment open in the garage so that it can air out.

- Plug in boat batteries to charge.

- Bill supplies and services for the week.

- Upload all photos to the Transfers folder. Create a folder for each site, named "FS-###" and name each photo so that it includes the FS number.

- When relinquishing samples to MPCA or MDH representative, complete "Relinquished by/Affiliation" along with date and time on lower part of Chain-of-Custody form. The accepting representative must complete the "Accepted by/Affiliation" portion of the form.

Field duplicates (10% of sites):

- Collect a complete duplicate set of cores and water samples from a site one canoe length away from your primary site. Treat as above, and label with a separate Location ID.

Field blanks (5% of sites):

- Rinse the brown plastic water sampling bottle three times with distilled or deionized water and then fill with the same water
- Subsample into water bottles exactly as for regular water subsamples and label as BLANK
- Record provenance of distilled water used (e.g., Civil Engineering Building low-purity DI, [brand name] commercial distilled water, etc.)
- Set up four clean, empty core tubes and sipping apparatus on extruder and lab stand. Fill with water used above. Sip as above and label with date, a separate Location ID, and BLANK in space for Site name/DOW number.

Decision tree for determining location to take cores at wild rice study sites

Ed Swain draft July 17, 2012

1	Site has wild rice.....2
	No wild rice evident.....3
2	Is a previously-cored site that has GPS location..... Core as close as possible to earlier site, in a wild rice bed.
	Is not a previously-cored site that has GPS location..... Choose a wild rice bed to sample in.
3	No aquatic macrophytes evident anywhere at the site (ignore cattails)..... Note lack of macrophytes and take reconnaissance samples (UA-1). Don't take sediment samples.
	Aquatic macrophytes evident at the site.....4
4	White or yellow water lily pads present……. Core in midst of the lily pads, noting lily species.
	White or yellow water lily pads not present……5
5	Other floating-leaved macrophytes (ignore duckweed) present……. Choose a bed of such plants, sample, and take a voucher plant of the major type for identification.
	Other floating-leaved macrophytes (ignore duckweed) not present……..6
6	Submerged macrophytes present…… Choose a site in about 3 feet of water or less and sample. Take a voucher plant of the major type for identification.
	Submerged macrophytes not present……7
7	Only emergent macrophytes (ignore cattails) present……. Choose a site in about 3 feet of water or less and sample. Take a voucher plant of the major type for identification.

Field sampling data sheet **MCPA/LacCore SO4 project** **Revision 2.7, 8/14/2012** **CF**

DNR ID

Lake ID

LacCore ID AIS status ○ Yes ○ No Hydrolab_calibrate ○ Yes ○ No

Water level ○ m ○ ft Benchmark location

Sediment probe observations surface

depth

Thermal stick deployed ○ Yes ○ No Time in: Time out:

Date (mm/dd/yyyy) Time (24 hr) Air temp ○ °C ○ °F

Crew member Wind

Crew member

Others present

Weather Flow conditions

Water quality sonde ○ Hach 1 ○ Hach 13 ○ Quanta GPS_devic ○ 1 ○ 2 ○ 3 Boat ○ Canoe ○ Motorboa

Location

Boat orientation ○ N ○ NE ○ E ○ SE ○ S ○ SW ○ W ○ NW Photos_taken ☐ Map/Site ☐ N ☐ E ☐ S ☐ W

Latitude Longitude lat/long type ☐ Exact ☐ Approximat ☐ Genera

Elevation_core ○ m ○ ft Accuracy ○ m ○ ft Waypoint_core

Temperature ○ °C ○ °F spC ○ mS/cm ○ uS/cm pH

Secchi depth ○ m ○ ft Secchi water depth ○ m ○ ft

Water sample_taken ○ Yes ○ No Rinse core tubes ○ Yes ○ No Collect cores ○ Yes ○ No

Repository core total length ○ cm ○ in Repository core sediment length ○ cm ○ in

Comments on location

Plant rings

	Name	Ring 1	Name	Ring 2	Name	Ring 3	Name	Ring 4
% Wild Rice								
# wild rice stems								
% submergent								
% floating leaf								
% emergent								
% sp.:								
% sp.:								
% sp.:								
% sp.:								
% sp.:								

Plant ring ☐ Photo 1 ☐ Photo 2 ☐ Photo 3 ☐ Photo 4

photo_taken

Comments_taxa_site

Rice Notes

% Open water in sight _____

2 mature wild rice plants collected for pressing ○ Yes ○ No

Comments_plant

Shore Processing

Pore water sippers

Sulfide vial weight (g) _____

☐ 70 mL ☐ 50 mL ☐ 50 mL ☐ 30 mL

Composite mud sample

Pore water pH _____

AVS preservative added ○ Yes ○ No

AVS stored on dry ice ○ Yes ○ No

composite jar_FS_collected ○ Yes ○ No

Sediment description ☐ organic ☐ sand ☐ fine ☐ coarse ☐ shells ☐ gassy

Sediment color _____

Water subsampling

250 mL Metals ○ Yes ○ No

250 mL General ○ Yes ○ No

250 mL Nutrients (w/H2SO4) ○ Yes ○ No

Hach color wheel

(with mirror) value = _____

(no mirror) value (x5) = _____

(no mirror + dilution) value (x10) = _____

T-tube

T-tube bottle shaken ○ Yes ○ No

T-tube Secchi depth disappear _____ ○ cm ○ in

T-tube Secchi depth appear _____ ○ cm ○ in

T-tube Secchi depth average _____ ○ cm ○ in

rhizons_used _____ Decontamination _____ AIS Label_added ○ Yes ○ No

Comments_general

File photo backup ○ Yes ○ No

Data_uploade ○ Yes ○ No

Billed ○ Yes ○ No

Daily report_sent ○ Yes ○ No

Complete MDH COC form ○ Yes ○ No

Plants_pressed ○ Yes ○ No

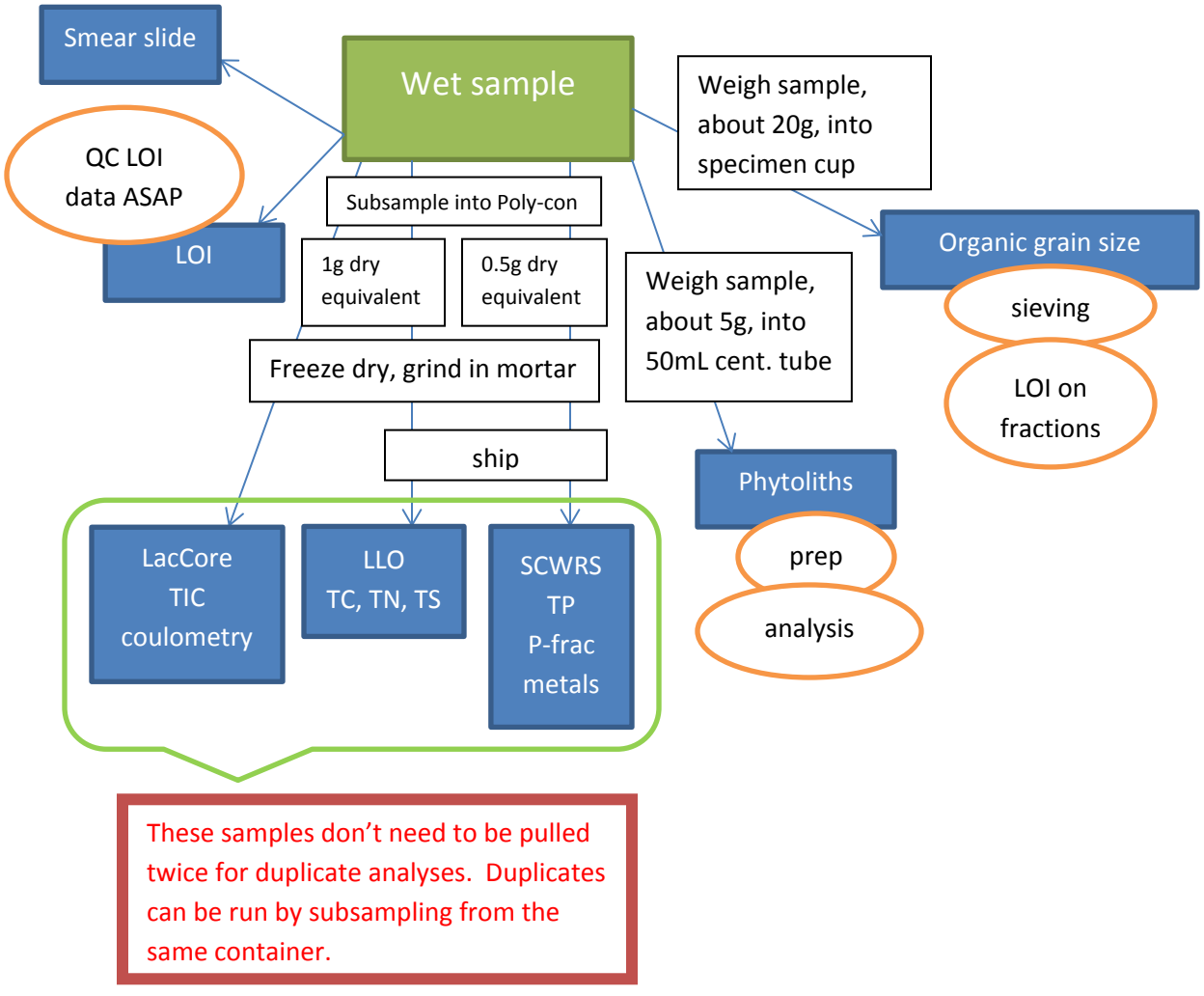
Appendix C

Overview protocol for SO4 sediment sample processing

11/7/11 (original)
10/18/12 **Draft:** revised by Amy to reflect 2012 protocol
10/19/2012 revised by Amy after discussion w/lab staff
11/3/12 revised by Amy to change protocol for freeze died samples

IMPORTANT:

Use FS- number AND site name on all labels
Tare balance for sample container
HOMOGENIZE FOR WATER CONTENT AND SEDIMENT TEXTURE BEFORE ALL SUBSAMPLING
Record all information, including sample weights, into database



Subsample 11 sites for duplication of all analyses (same spls for all) (but see comment directly above to left) – Amy/Ed will select

Appendix D. Summary data from the sites sampled in 2011 and 2012.

Complete data can be obtained from the Minnesota Pollution Control Agency.

Explanation of Field Names in Appendix D

Site Name: The name of the lake, stream, or wetland. When possible, the name established by the Minnesota DNR is used that corresponds to the state location ID. If a cultivated rice paddy was sampled, the site name is listed as "Rice paddy."

County: The county in which the site is located, or if a lake is large, the county that the Minnesota DNR assigns to the state location ID.

State Location ID: The state's location identification numbers correspond to lakes, wetlands, or streams. Stream numbers start with an "S". Cultivated rice paddies were assigned a wetland ID, which starts with "WT".

LacCore Site ID: LacCore staff, who conducted the field surveys, assigned a site ID for each sample visit. LacCore site IDs assigned during the 2011 preliminary survey start with a "P". Site IDs assigned during the 2012 field survey start with "FS".

Collect cores?: If sediment cores were collected during a site visit, "Yes" is listed.

Date Site Visit: The date of the site visit is given.

Porewater pH: After sediment cores are transported to shore for processing, the pH of the porewater is measured by inserting a pH probe 5 cm into a core.

Surface water pH: The pH of the water at the sampling site, just below the surface, as measured with a field Sonde.

Surface water Conductivity (micro S/cm): The conductivity of the water at the sampling site, just below the surface, as measured with a field Sonde, corrected to 25°C.

Surface water temp C: The temperature of the water at the sampling site, just below the surface, as measured with a field Sonde.

Wild rice in plant rings (average % cover): The average percent cover, as estimated by the field crew in 4 1-m diameter rings dropped over the side of the boat at the sediment coring site.

Site Name	County	State Location ID	LacCore Site ID	Collect cores?	Date Site Visit	Porewater pH	Surface water pH	Surface water Conductivity (micro S/cm)	Surface water temp C	Wild rice in plant rings (average % cover)
Anka	Douglas	21-0353-00-202	P-34		09/16/2011	7.2	8.0	370	15.5	11
Anka	Douglas	21-0353-00-202	FS-192	Yes	08/29/2012	6.8	8.4	441	32.9	1
Bass	Itasca	31-0576-00-207	FS-134	Yes	09/18/2012	7.6	8.1	266	13.4	33
Bean	Becker	03-0411-00-201	FS-85	Yes	08/21/2012	7.3	9.8	411	20.2	0
Bear	Freeborn	24-0028-00-206	FS-178	No	07/25/2012		8.7	297	27.7	
Bee	Polk	60-0192-00-202	FS-87	Yes	08/23/2012	6.9	8.7	370	25.3	19
Big Mud	Sherburne	71-0085-00-201	FS-193	Yes	08/30/2012	6.5	7.4	233	24.1	4
Big Sucker	Itasca	31-0124-00-203	FS-216	Yes	09/12/2012	6.4	7.3	201	17.9	1
Big Swan	Todd	77-0023-00-208	FS-204	Yes	08/10/2012	6.4	7.5	362	23.9	55
Big Swan	Todd	77-0023-00-207	FS-205	Yes	08/10/2012	6.6	7.7	357	27.1	18
Birch	Saint Louis	69-0003-00-205	P-12		08/30/2011	5.6	7.5	92	20.3	30
Birch	Saint Louis	69-0003-00-205	FS-89	Yes	09/10/2012	6.9	7.0	104	19.0	26
Blaamyhre	Kandiyohi	34-0345-00-203	FS-52	Yes	08/01/2012	6.9	8.2	326	28.5	15
Bowstring	Itasca	S007-219	FS-214	Yes	09/11/2012	6.7	7.3	226	17.3	28
Bray	Otter Tail	56-0472-00-202	FS-126	Yes	08/20/2012	6.6	9.4	229	24.6	2
Caribou	Saint Louis	69-0489-00-205	P-32		09/15/2011		8.7	120	18.2	0
Caribou	Saint Louis	69-0489-00-206	FS-63	Yes	09/03/2012	6.1	8.7	130	28.1	0
Clearwater	Clearwater	S004-204	FS-88	Yes	08/24/2012	7.2	7.3	515	21.2	61
Clearwater	Clearwater	S002-121	FS-189	Yes	08/28/2012	7.6	8.0	490	20.9	2
Cloquet	Lake	38-0539-00-201	P-31		09/14/2011	6.0	7.2	59	12.7	33
Cromwell	Clay	14-0103-00-201	FS-128	Yes	08/22/2012	7.0	9.6	591	23.7	0
Dead Fish	Carlton	09-0051-00-202	P-44		09/20/2011	6.3	7.7	196	12.8	21
Dead Fish	Carlton	09-0051-00-202	FS-64	Yes	09/04/2012	7.5	7.4	156	23.8	0
Eighteen	Polk	60-0199-00-202	FS-86	Yes	08/22/2012	6.8	8.6	395	24.8	24
Elk	Clearwater	15-0010-00-204	P-6		08/25/2011	6.4	7.2	231	22.8	11
Elk	Clearwater	15-0010-00-204	FS-137	Yes	09/19/2012	7.8	9.2	273	16.5	7
Embarrass	Saint Louis	69-0496-00-202	P-9		08/29/2011		8.0	170	21.6	0
Embarrass	Saint Louis	69-0496-00-203	FS-95	Yes	09/14/2012	7.8	8.0	196	17.1	0
Field	Kandiyohi	34-0151-00-201	FS-76	Yes	07/25/2012	6.8	8.5	177	27.4	0
Fisher	Scott	70-0087-00-201	FS-195	Yes	08/31/2012	6.5	8.3	564	28.5	25
Flowage	Aitkin	01-0061-00-205	P-51		09/22/2011	6.4	7.3	155	11.7	70
Flowage	Aitkin	01-0061-00-206	P-52		09/22/2011					54
Flowage	Aitkin	01-0061-00-204	FS-81	Yes	08/07/2012	6.5	6.9	124	25.5	0
Gilchrist	Wright	86-0064-00-201	FS-194	Yes	08/31/2012	6.5	7.4	337	22.9	0
Glesne Slough	Kandiyohi	34-0353-00-201	FS-51	Yes	07/31/2012	6.7	7.2	513	25.6	23
Gourd	Beltrami	04-0253-00-201	P-23		09/07/2011	6.7	7.0	235	20.7	17
Gourd	Beltrami	04-0253-00-201	FS-104	Yes	06/27/2012		6.3	254	24.2	
Grand	Saint Louis	69-0511-00-203	P-39		09/17/2011		9.3	126	13.1	0
Gull	Beltrami	04-0120-00-204	P-20		09/06/2011	6.9	7.0	177	19.4	7
Gull	Beltrami	04-0120-00-204	FS-213	Yes	09/10/2012	6.3	7.3	226	14.9	5
Ham	Anoka	02-0053-00-201	P-22		09/06/2011		7.6	290	21.8	0
Hay	Itasca	31-0037-00-202	P-45		09/21/2011	6.6	8.3	388	13.1	0
Hay	Itasca	31-0037-00-203	P-46		09/21/2011	6.7				0
Hay	Itasca	31-0037-00-202	FS-130	Yes	09/06/2012	7.5	8.0	434	19.5	54
Hay Creek Flowage	Pine	58-0005-00-202	FS-221	Yes	09/17/2012	6.4	7.1	258	17.8	59
Height of Land	Becker	03-0195-00-210	P-1		08/22/2011	6.9	8.7	234	22.2	28
Height of Land	Becker	03-0195-00-210	FS-127	Yes	08/21/2012	7.1	7.9	313	21.0	70
Hinken Creek	Itasca	S007-207	FS-131	Yes	09/05/2012	6.9	7.5	276	21.3	19
Hoffs Slough	Swift	76-0103-00-201	FS-185	Yes	08/01/2012	6.7	7.8	1030	21.2	0
Holman	Itasca	31-0227-00-202	FS-218	Yes	09/13/2012	6.7	7.7	355	15.9	0
Hunt	Rice	66-0047-00-208	FS-182	Yes	07/27/2012	7.9	9.4	274	27.3	0
Ina	Douglas	21-0355-00-201	P-37		09/16/2011		7.8	420	17.7	0
Ina	Douglas	21-0355-00-202	FS-191	Yes	08/29/2012	6.7	8.6	379	23.3	9
Itasca	Clearwater	15-0016-00-208	P-5		08/25/2011	6.8	8.7	266	22.9	20
Itasca	Clearwater	15-0016-00-207	P-7		08/25/2011	6.5				9
Itasca	Clearwater	15-0016-00-208	FS-136	Yes	09/19/2012	8.1	9.4		16.3	8
Kelly Lake	Rice	66-0015-00-204	FS-207	Yes	08/13/2012	6.1	8.8		27.7	0
Lady Slipper	Lyon	42-0020-00-204	P-55		09/22/2011	7.5	8.7	1082	13.6	0
Lady Slipper	Lyon	42-0020-00-202	FS-78	Yes	07/27/2012	7.4	9.2	1136	25.1	0
Lady Slipper	Lyon	42-0020-00-203	FS-79	Yes	07/27/2012	7.3	9.3	1125	26.4	0
Lax	Lake	38-0406-00-203	P-18		09/02/2011		7.9	79	21.4	0
Lily	Waseca	81-0067-00-203	P-61		09/28/2011	6.4	7.2	316	16.2	23
Lily	Waseca	81-0067-00-203	P-62		09/28/2011					0
Lily	Waseca	81-0067-00-202	FS-180	Yes	07/26/2012	6.2	6.9	305	26.8	19
Little Birch	Todd	77-0089-00-208	P-47		09/21/2011	6.5	7.4	348	16.4	11
Little Birch	Todd	77-0089-00-207	FS-54	Yes	08/03/2012	6.7	8.6	312	26.5	11
Little Flat	Becker	03-0217-00-201	P-4		08/24/2011	6.5	8.1	392	23.1	36
Little Rice	Saint Louis	69-0612-00-201	FS-250	Yes	09/20/2012	6.0	6.7	50	11.3	9
Little Round	Becker	03-0302-00-204	P-3		08/24/2011	6.5	7.7	284	21.8	25
Little Round	Becker	03-0302-00-203	FS-138	Yes	09/20/2012	7.8	8.7	467	13.7	46
Little Sucker	Itasca	31-0126-00-202	FS-223		09/14/2012	6.7	7.2	261	16.0	0
Long Prairie	Douglas	S007-204	FS-202	Yes	08/09/2012	7.2	7.5	456	21.9	9
Long Prairie	Douglas	S007-203	FS-203	Yes	08/09/2012	7.3	7.7	465	22.8	46

Site Name	County	State Location ID	LacCore Site ID	Collect cores?	Date Site Visit	Porewater pH	Surface water pH	Surface water Conductivity (micro S/cm)	Surface water temp C	Wild rice in plant rings (average % cover)
Louisa	Wright	86-0282-00-205	FS-200	Yes	08/08/2012	6.6	7.6	427	22.3	0
Louise	Douglas	21-0094-00-202	FS-226	Yes	08/14/2012	8.0	8.7	366	23.6	17
Lower Panasa	Itasca	31-0112-00-202	FS-140	Yes	08/29/2012	6.6				
Lower Panasa	Itasca	31-0112-00-202	FS-60	No	08/29/2012		8.7	329	26.2	0
Lower Rice	Clearwater	S006-985	P-25		09/08/2011	7.2	7.2	323	18.1	50
Lower Rice	Clearwater	S006-985	P-26		09/08/2011	6.8	6.8	325	19.0	53
Maloney	Wabasha	79-0001-00-201	P-63		09/29/2011	6.4	7.3	617	17.1	65
Maloney	Wabasha	79-0001-00-201	P-64		09/29/2011					0
Maloney	Wabasha	79-0001-00-201	FS-175	Yes	07/23/2012	6.7	7.2	435	30.6	0
McCormic	Stearns	73-0273-00-203	FS-187	Yes	08/02/2012	7.4	9.5	274	27.5	1
Menomin	Crow Wing	18-0126-02-201	FS-133	Yes	09/17/2012	7.1	9.0	349	18.1	0
Mill Pond	Douglas	21-0034-00-202	FS-229	Yes	08/16/2012	6.7	7.6	495	21.1	30
Mill Pond	Douglas	21-0034-00-202	FS-230	Yes	08/16/2012	6.9	7.7	491	22.3	22
Miltona	Douglas	21-0083-00-205	FS-225		08/13/2012		8.5	326	24.8	0
Miltona	Douglas	21-0083-00-205	FS-227		08/14/2012	6.9				
Mink	Wright	86-0229-00-206	FS-201	Yes	08/08/2012	7.0	9.6	262	24.9	0
Mink	Wright	86-0229-00-207	FS-129	Yes	08/23/2012	6.3	7.5	267	23.1	0
Mission	Pine	S001-646	FS-80	Yes	08/06/2012	6.8	7.1	239	21.9	52
Mississippi	Becker	S007-163	P-14		09/01/2011	6.6	7.8	251	21.3	71
Mississippi	Itasca	S006-923	P-15		09/01/2011	6.6	7.6	255	22.2	44
Mississippi	Itasca	S006-923	FS-57	Yes	08/28/2012	7.4	7.6	293	25.6	0
Mississippi	Becker	S007-163	FS-58	Yes	08/28/2012	7.2	7.7	266	24.7	0
Mississippi (Crow Wing)	Crow Wing	S007-205	FS-83	Yes	08/08/2012	6.9	7.6	234	24.4	0
Mississippi Pool 4/Robinson Lake	Wabasha	79-0005-02-202	FS-210	Yes	08/16/2012	6.7	7.1	339	21.3	21
Mississippi Pool 4/Robinson Lake	Wabasha	79-0005-02-201	FS-211	Yes	08/16/2012	7.0	7.2	310	22.2	51
Mississippi Pool 5 / Spring	Houston	S007-221	FS-212	Yes	08/17/2012	7.9	9.2	292	21.2	18
Mississippi Pool 8 at Genoa	Houston	S007-222	FS-208	Yes	08/14/2012	7.1	8.1	342	27.6	44
Mississippi Pool 8 at Reno Bottoms	Houston	28-0005-00-201	FS-209	Yes	08/15/2012	6.8	7.6	344	24.1	46
Monongalia	Kandiyohi	34-0158-01-202	P-42		09/20/2011	6.5	6.9	680	13.0	3
Monongalia	Kandiyohi	34-0158-02-204	FS-77	Yes	07/26/2012	7.4	8.2	347	28.4	39
Mortenson	Kandiyohi	34-0150-02-201	FS-75	Yes	07/24/2012	6.9	7.9	262	27.9	0
Mud	Otter Tail	S004-735	P-2		08/23/2011		8.4	350	24.1	0
North Geneva	Freeborn	24-0015-00-209	FS-176	Yes	07/24/2012	6.7	8.9	298	30.1	0
Ox Hide	Itasca	31-0106-00-203	FS-132	Yes	09/07/2012	6.8	8.0	373	20.3	4
Ox Hide	Itasca	31-0106-00-203	FS-198	Yes	09/07/2012	7.0	7.9	373	20.0	0
Padua	Stearns	73-0277-00-203	P-29		09/13/2011	6.2	7.3	271	18.6	2
Padua	Stearns	73-0277-00-202	FS-220	Yes	08/07/2012	6.4	9.2	314	25.3	0
Partridge	Sibley	S002-599	P-13		08/31/2011	6.6	6.4	191	19.4	29
Partridge	Sibley	S002-599	FS-92	Yes	09/12/2012	7.4	7.8	260	16.0	2
Pelican	Grant	26-0002-00-219	P-8		08/26/2011					0
Pelican	Grant	26-0002-00-219	P-33		09/15/2011		8.5	363	18.3	0
Pelkey	Morrison	49-0030-00-202	FS-55	Yes	08/26/2012	6.7	9.4	208	29.6	0
Pike	Sibley	S006-927	P-10		08/30/2011	6.6	7.0	172	21.8	19
Pike	Sibley	S006-927	P-10		08/30/2011	6.6	7.0	172	21.8	19
Pike	Sibley	S006-927	FS-91		09/11/2012	6.8	7.5	215	19.9	24
Pine	Clearwater	15-0149-00-205	FS-190	Yes	08/28/2012	6.6	8.6	369	26.4	48
Pleasant	Cass	11-0383-00-207	P-27		09/09/2011	6.3	7.6	171	21.4	13
Pleasant	Cass	11-0383-00-207	FS-84	Yes	08/10/2012	6.3	7.3	210	20.7	0
Pool 9	Anoka	02-0504-00-202	P-53		08/19/2011	6.5	6.8	187	23.5	19
Pool 9	Anoka	02-0504-00-202	FS-109	Yes	07/03/2012	5.9	5.9	200	27.7	24
Popple River	Itasca	S006-188	FS-215	Yes	09/11/2012	6.7	7.8	258	19.3	12
Prairie	Itasca	S007-209	FS-196	Yes	09/03/2012	6.4	7.7	196	26.6	16
Rabbit	Crow Wing	18-0093-02-204	FS-82	Yes	08/08/2012	6.8	7.5	272	22.9	0
Raymond	Stearns	73-0285-00-203	P-28		09/12/2011	7.3	7.6	333	22.8	30
Raymond	Stearns	73-0285-00-203	FS-53	Yes	08/02/2012	7.0	4.0	284	30.8	19
Rice	Crow Wing	18-0053-00-203	P-56		09/23/2011		7.6	276	11.6	0
Rice	Crow Wing	18-0053-00-203	P-69		09/27/2011	6.4	7.2	224	17.7	19
Rice	Steele	74-0001-00-201	FS-179	Yes	07/25/2012	7.2	9.3	204	31.0	0
Rice	Rice	66-0048-00-203	FS-181	Yes	07/27/2012	6.9	7.1	330	23.3	0
Rice	Stearns	73-0196-00-216	Fs-184	Yes	07/30/2012	6.6	9.5	278	31.5	0
Rice	Crow Wing	18-0053-00-203	FS-56	Yes	08/27/2012	6.5	7.4	234	20.9	4
Rice	Anoka	02-0008-00-206	FS-231	Yes	08/17/2012	6.7	9.3	351	23.1	0
Rice paddy	Pennington	WT00026	FS-101	Yes	06/25/2012	5.4	7.2	229	23.7	4
Rice paddy	Pennington	WT00027	FS-102	Yes	06/26/2012	6.2	6.4	897	21.4	39
Rice paddy	Pennington	WT00028	FS-103	Yes	06/26/2012	6.3	8.6	927	27.9	24
Rice paddy	Clearwater	WT00029	FS-106	Yes	06/28/2012	5.9	7.8	434	22.1	25
Rice paddy	Clearwater	WT00030	FS-107	Yes	06/28/2012	6.2	7.2	489	24.2	80
Rice paddy	Crow Wing	WT00031	FS-108	Yes	06/29/2012	5.9	7.3	132	23.0	34
Rice River	Itasca	S006-208	FS-199	Yes	09/05/2012	7.3	7.5	247	19.1	29
Sand	Sibley	S003-249	P-11		08/30/2011	6.5	6.5	228	19.6	6
Sand	Sibley	S003-249	FS-90	Yes	09/11/2012	7.2	7.7	322	15.7	1
Sandy	Saint Louis	69-0730-00-203	FS-251	Yes	09/21/2012	7.0	6.5	120	12.0	1
Second	Clearwater	15-0091-00-202	P-24		09/07/2011	6.6	7.7	252	24.1	16

Site Name	County	State Location ID	LacCore Site ID	Collect cores?	Date Site Visit	Porewater pH	Surface water pH	Surface water Conductivity (micro S/cm)	Surface water temp C	Wild rice in plant rings (average % cover)
Second	Clearwater	15-0091-00-202	FS-105	Yes	06/27/2012	5.8	8.1	265	32.4	13
Snowball	Itasca	31-0108-00-202	FS-197	Yes	09/04/2012	6.2	8.4	211	22.3	0
South Geneva	Freeborn	24-0015-00-208	FS-177	Yes	07/24/2012	6.4	8.7	306	32.0	0
St. Louis	Sibley	S006-929	P-16		09/01/2011	6.9	6.7	343	19.8	0
St. Louis	Sibley	S006-929	P-17		09/01/2011	6.0	6.4	11	19.0	30
St. Louis	Sibley	S007-208	FS-69	Yes	09/07/2012	6.5	6.9	75	17.7	0
St. Louis	Sibley	S006-929	FS-70	Yes	09/07/2012		7.8	349	16.2	0
St. Louis Estuary	Sibley	S006-926	P-40		09/19/2011		8.3	208	18.1	0
St. Louis Estuary	Sibley	S007-206	FS-66	Yes	09/05/2012	7.3	8.1	226	21.9	0
St. Louis Estuary Pokegama Bay	Douglas Co., Wisconsin	S006-928	P-41		09/19/2011		7.9	178	17.9	0
St. Louis Estuary Pokegama Bay	Douglas Co., Wisconsin	S006-928	FS-67	Yes	09/05/2012	6.9	8.1	211	25.4	0
Stella	Meeker	47-0068-00-205	P-30		09/14/2011	5.9	7.9	374	20.5	14
Stella	Meeker	47-0068-00-204	FS-188	Yes	08/27/2012	6.9	8.7	337	26.0	0
Stone Lake	Saint Louis	69-0046-00-201	FS-224	Yes	09/19/2012	6.3	7.5	105	13.0	6
Sturgeon	Saint Louis	S004-870	FS-94	Yes	09/13/2012	6.9	7.0	98	15.0	14
Swan	Kandiyohi	34-0223-00-203	FS-50	No	07/30/2012		8.1	429	28.4	
Swan	Itasca	31-0067-02-206	FS-61	Yes	08/30/2012	6.6	7.8	299	23.6	3
Swan	Itasca	31-0067-02-206	FS-62	Yes	08/30/2012	6.5	8.3	301	26.8	1
Tamarac	Otter Tail	56-0192-00-203	FS-125	Yes	08/19/2012	6.5	8.8	300	27.8	0
Trout	Itasca	31-0216-00-212	FS-219	Yes	09/13/2012	6.6	8.7	325	19.7	0
Turpela	Saint Louis	69-0427-00-201	FS-93	Yes	09/12/2012	7.3	7.7	176	18.8	1
Unnamed	Kandiyohi	34-0611-00-201	P-57		09/23/2011	6.9	7.7	362	16.9	33
Unnamed	Kandiyohi	34-0611-00-201	FS-183	Yes	07/30/2012	6.7	8.6	360	25.4	16
Upper Panasa	Itasca	31-0111-00-202	FS-59	Yes	08/29/2012	7.4	8.7	345	23.1	0
Welby family farm	Wright	86-0237-00-202	FS-139	Yes	09/21/2012	7.0	8.3	342	14.8	2
West battle	Otter Tail	56-0239-00-204	FS-228	Yes	08/15/2012	6.9	8.6	330	25.8	35
Westport	Pope	61-0029-00-204	FS-186	Yes	08/01/2012	7.5	8.9	311	27.2	0
Wild Rice	Carlton	09-0023-00-201	P-43		09/20/2011		7.2	130	12.6	
Wild Rice	Carlton	09-0023-00-202	FS-65	Yes	09/04/2012	6.6	6.8	107	26.3	0
Wild Rice Reservoir	Saint Louis	69-0371-00-203	P-36		09/16/2011	5.5	8.1	111	12.9	8
Wolf	Saint Louis	69-0143-00-203	P-19		09/02/2011	5.8	6.5	18	20.8	56
Wolf	Saint Louis	69-0143-00-101	FS-68	Yes	09/06/2012	6.3	6.8	57	20.7	2

Appendix E. Standard operating procedures (SOPs)

Loss-on-ignition (LOI)

Total inorganic carbon (TIC) coulometry

Total sulfur (TS) coulometry

Total carbon and total nitrogen elemental analysis (TC/TN)

Loss-on-Ignition

Purpose
Water, organic matter, carbonate mineral, and siliciclastic+diatom content are estimated by sequentially measuring weight loss in sediment core subsamples after heating at selected temperatures.

A compositional profile can be generated rapidly and for very low cost. This profile is sufficient to develop a general sense of core stratigraphy and often is sufficient for correlation between cores.

The results are accurate to 1-2% for organic matter and carbonate in sediment with over 10% organic matter. In clay- or diatom-rich sediment, water of hydration is lost during the carbonate burn, resulting in errors of up to 5% for carbonate analyses (and "false positive" carbonate content in carbonate-free sediments). If high precision (0.1%) is needed, or if sediment is in short supply, coulometric analysis is recommended.

A nonprogrammable Lab Line L-C oven is used for the 100ºC drying step. Other drying ovens are also available in the lab. A drying oven rather than a furnace is used for the 100°C step because the furnaces ramp up to temperature quickly and may overshoot 100°C by an amount that could affect the analysis.

A Fisher Scientific Isotemp programmable muffle furnace is used for the 550°C and 1000°C steps. This is a multiple mode instrument capable of reaching 1125°C and controlling temperatures to better than ± 15ºC with a ± 10ºC temperature uniformity. The programmable circuit will provide the necessary corrections to maintain temperatures at established set point. This furnace holds 200 samples at a time. Another furnace, the Lindberg Blue M, is available for use as a backup, but only holds 50 samples. This is a 2 mode instrument capable of controlling temperatures to better than ± 10ºC. The automatic reset circuit will provide the necessary corrections to maintain temperatures at established set point.

Procedure Summary
Subsamples are placed in weighed crucibles and weighed. Weight loss is measured after heating at 100ºC overnight to remove water, at 550ºC for four hours to remove organic matter, and at 1000ºC for two hours to remove carbonates. After each heating step, the firebrick holding crucibles is allowed to cool completely in the oven or furnace before weighing, or placed in a desiccator if crucibles cannot be weighed immediately. Samples must be cool so that convection currents do not affect the balance, and kept in the oven, furnace, or desiccator so that they do not absorb atmospheric water. Samples must not be placed in a non-venting desiccator when warm.

Ash left at the end of the procedure can be saved for analysis of remaining elements as oxides.

Only one heating step can be accomplished each day, because the 100°C drying time, and the ramp-up and cool-down times of the furnaces are all >8-10 hours. The user should thus plan five days, ideally consecutively:
Day 1 Weigh crucibles (if necessary), subsample, and weigh (initial or wet weightt); place samples in drying oven at *100°C* (allow several hours for these steps, depending on subsampling complexity).
Day 2 Turn off oven, let samples cool, weigh (100°C, dry weight, or water loss); place samples in furnace at *550°C for 4 hr* (about 0.5-1 hour per tray of 25 samples).
Day 3 Weigh (550°C or organic matter loss); place samples in furnace at *1000°C for 2 hr* (about 0.5-1 hour per tray of 25 samples).
Day 4 Weigh (1000°C or carbonate loss), discard or save sample residues, wash crucibles, place crucibles back in trays, place trays of crucibles in furnace at 1000°C for 2 hours to completely clean the crucibles.

Day 5 Turn off oven, allow crucibles to cool completely, remove trays from drying oven, cover with foil, and place in desiccator for reuse (1-2 hr). Label these trays as clean and ready to be reused.

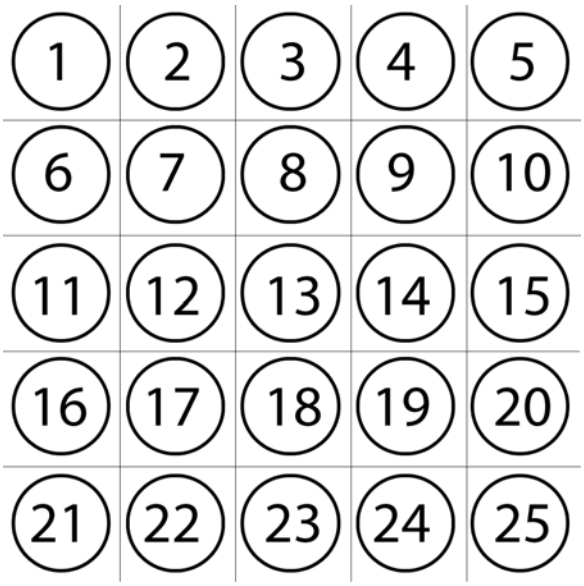
Equipment
Ceramic crucibles
Firebricks drilled to accept crucibles
Sampling device (spatula, syringe)
Desiccator(s)
Drying oven
Muffle furnace capable of reaching 1000°C
Balance weighing in grams to 4 decimal places

Safety
The most obvious hazard in LOI is being burned by hot samples fresh out of the furnace. Be patient. The high-temp gloves and mitts are only good to about 350°C and can be awkward to use.

The muffle furnaces each have a thermocouple (looks like a white stick with metal protruding from the end) which penetrates in through the back of the chamber. It is easily damaged, so be careful not to bump it when adding or removing samples.

Procedure Detail
1. Select and weigh 25 crucibles per fire brick tray. You can prepare up to 200 samples (eight trays) for analysis at a time.
    a. Never touch crucibles with your hands. Skin oils will add weight and introduce error to your results. Always use a pair of tweezers when handling crucibles.
    b. The crucibles are numbered with permanent glaze. Check to see that they are in order in the brick (see below) and that you are starting with the lowest numbered crucible in your tray. Keep good notes! As soon as you've mixed things up the data are useless.
    c. When not burning or being weighed, the crucibles and the samples they contain must be stored in a desiccator. Make sure there is enough desiccator space for the number of samples you hope to analyze. Wait until the samples are cool (<30°C) before putting them in the desiccator: the decrease in pressure upon cooling of the air in the desiccator will vacuum-seal the desiccator shut and it'll be very difficult to open.
    d. Always remove aluminum foil before placing trays in drying oven or furnace
2. Record your crucible weights in the LOI template spreadsheet [*saved in transfers/SOPs/ as* **LOI.Template.xls**]. This new template will highlight (in red) any weights entered that are clearly incorrect (i.e., less than or equal to the empty crucible weight or greater than or equal to the weight of the preceding burn).
3. Place some sample (~1-5 cc) in each crucible and weigh. Weighing should be done as soon as each tray is filled, do not wait to fill multiple trays before weighing. This is your *wet weight*. Record in LOI spreadsheet. *Note:* if you use the **LOI macro** (more about which later), the samples do not have to be volumetric.
4. Heat these samples at **100-105°C overnight or for at least 12 hours in** the drying oven. This will evaporate water and the resulting weight will be your *100°C weight*. Let samples cool in the oven, until <30°C, before weighing. If you cannot weigh the samples immediately after they cool, place in a desiccator with aluminum foil between each tray until you can weigh them.

5. After weighing and recording your *100°C weight*, return the samples to the furnace for a **4-hour burn at 550°C**. This will burn off organic matter. The following day, after samples have cooled in the furnace, samples can be weighed. If you cannot weigh the samples immediately after they cool, place in a desiccator with aluminum foil between each tray until you can weigh them. This will allow samples to take in air moisture and throw off your weights. See furnace directions below.
6. Record your post-550 burn weights in the spreadsheet and return the samples to the oven for a **2-hour 1000°C** burn. This will burn off a combination of carbonate material and some of the water stored in the lattice of clay minerals and diatom silica. See furnace directions below.
7. After cooling, record this weight as your final measurement. You may discard the sample remaining in the crucible, or save it for another analysis.
8. Run the LOI Macro. See directions below.
9. Clean the crucibles for the next user.
    a. Two buckets are needed and should be in or near the sink in room 680A. Fill one bucket with warm tap water and add soap from the bottle labeled "Lab Soap" above the sink. Fill the other bucket with low-purity deionized water from carboy above the adjacent sink.
    b. Remove any remaining residue and place the crucibles in the warm tap-water bath.
    c. Using a brush found above the sink, scrub the crucibles until all baked on residue is gone. Some discoloration will remain.
    d. Rinse the crucibles in the DI water bath, shake dry and place in the firebrick tray following the numbering system designated in the figure on the right.



    e. Place all washed trays of crucibles in the furnace and burn at 1000°C for two hours (in the same manner as the carbonate burn).
    f. The following day, remove all trays from the furnace, cover with aluminum foil and place in appropriate desiccators. Use the "Cleaned 1000°C" crucible icons or label the trays "Cleaned and burned at 1000°C" between each tray so that the next person knows they are ready to be used.

How to use the Lab Line L-C oven

1. Open the oven and place your trays on the shelving in the oven. Load in the top trays first to prevent contamination of the samples. Close the oven door
2. Turn on the oven using the switch on the front panel.
3. Set the temperature knob about ¾ of the way between a setting of 4 and 5 to heat the oven to 100°C.
4. The oven does not have a temperature feedback control system, it is a good idea to periodically check the temperature on the oven to make sure it reaches 100°C but does not greatly exceed 100°C.

How to use the Isotemp muffle furnace in Ramp and Soak mode

1. Open the flue on top of the furnace.
2. Turn on the Furnace using the switch on the front control panel.
3. Open the furnace and place your trays on the shelving in the furnace. Load in the top trays first to prevent contamination of the samples. The muffle furnace has a thermocouple (looks like a white stick with metal

protruding from the end) which sticks in through the back of the chamber. It is easily damaged, so be careful when adding or removing samples not to bump it. Close the furnace door.

4. Verify that the Run LED is not on. If it is on, press Run until the light goes out.
5. Press the following sequence of buttons in the left most column.

Button	Top Display	Lower Display	Description
Menu	No	program	Furnace is not in program mode.
UP	Yes	program	Select yes to set program parameters
Menu	1	step	The first step in the program
Menu	SP (Set Point)	styp (step type)	is a set point.
Menu	(550 or 1000)°C	sp	This is the temp from the last time the program ran.
Up/Down	(550 or 1000)°C	sp	Use the up or down keys to set to 550 or 1000°C.
Menu	20° C	rate	The ramp up rate should always be 20°C for LOI.
Menu	No	retn (return)	No return for this step,
Menu	2	step	move on to step two in the program,
Menu	Soak	styp	a soak step.
Menu	(4 or 2)	hour	This is the length from the last time the program ran
Up/Down	(4 or 2)	hour	Use the up or down keys to set to 2 or 4 hours,
Menu	0	min	0 minutes,
Menu	0	sec	0 seconds,
Menu	No	retn	No return for this step.
Menu	3	step	Move on to step three in the program,
Menu	end	styp	to end the program,
Menu	off	end	by letting the furnace cool to room temp.
Menu	yes	save	Save the program.
Menu	actual temp	set temp	You have exited the program parameters.

6. Press run twice to run the program, the run light should be solid (not flashing) and the program will automatically start to ramp up to temperature. You can see the set temperature and the actual temperature on the display.
7. Once the furnace has cooled down, you can close the flue and turn off the furnace. If the alarm LED is lit up on the control panel please notify staff, this means that the actual furnace temperature exceeded the set temperature by more than 25°C
8. Remove the bottom shelf of samples first, to prevent contamination.

How to use the LOI Macro

To use the macro [*saved in transfers/SOPs/LOI as* **LOI.Macro.xls**], the spreadsheet that contains your LOI data must be in the following format (column titles):

Depth, Crucible Weight, Wet Weight, Weight (100°C), Weight (550°C), Weight (1000°C)
or
Depth (Top), Depth (Bottom), Crucible Weight, Wet Weight, Weight (100°C), Weight (550°C), Weight (1000°C).

These columns and the data within them are the ONLY cells that may be filled in on the page, or the macro will malfunction. If you have supplementary data such as crucible number, core names, notes to self, etc., cut them from this spreadsheet and put them in another sheet in the same workbook.

Save the data spreadsheet as a **new file** (the macro overwrites the opened file) and close it. Open up the **LOI.Macro.xls** file. (Click “enable macros” in the warning window that pops up.) Go to Tools--> Macro--> Macros (or press Alt-F8). The "macro name" line should read "A1" and be highlighted. The first line of the section below A1 should read "LOI." Click "Run."

The next box that pops up asks for the file name (as saved on the spreadsheet), some info about the coring site (nonessential), whether your depth intervals are single or you've used two columns for top and base depths (determined by which format for column titles you used above), and whether you did a $CaCO_3$ (1000°C) burn. Once you've filled in and selected the appropriate options, click "OK" and the macro will perform its magic. It will probably not find your file at first, but you have the option of browsing for it.

The resulting data will be placed in columns to the right of your original data.

*For a comprehensive review of best practices and comparative LOI methods, please see Heiri et al, Journal of Paleolimnology 25, p. 101-110.

Total Inorganic Carbon (TIC, Carbonate) Coulometry

Total Inorganic Carbon coulometry (TIC) measures the amount of inorganic carbon contained in lake sediments or water samples. The TIC content of sediments can be related to a number of factors such as rates precipitation of carbonate minerals or introduction of detrital carbonates into the system. The LRC CO_2 Coulometer can be used to rapidly determine TIC from either water or sediment samples.

Principles

Carbon dioxide gas evolved by dissolution in acid from carbonates in the sample is swept by a gas stream into a coulometer cell. The coulometer cell is filled with a partially aqueous medium containing ethanolamine and a colorimetric indicator. Carbon dioxide is quantitatively absorbed by the solution and reacts with the ethanolamine to form a strong, titratable acid which causes the indicator color to fade. The titration current automatically turns on and electrically generates base to return the solution to its original color (blue).

Equipment and Procedure

To measure TIC, carbon contained within carbonate minerals such as calcite, dolomite, siderite, etc., we use a UIC model 5030 Carbonate Carbon apparatus. Five mL of acid (we prefer HCl) serves to evolve CO2 from the sample which is swept into the Carbon Coulometer where it is detected and displayed on a digital screen in terms of micrograms (or any other operator-selectable units) of carbon.

Cell Preparation

The coulometer cell is typically left set up (a change from the older procedure), so unless you are getting bad numbers, you should rarely have to clean or refill the cell.

Note: you must wear appropriate gloves when handling coulometry solutions. A pair of butyl rubber gloves hangs in the cabinet with the columetry solutions. For the rest of this procedure, you must wear regular lab gloves to protect your hands from the acid. Cell filling and cleaning must be done in a fume hood.

1. Fill the main chamber of the coulometer cell with 50-75 mL of cathode solution (large plastic bottle).

2. Place the magnetic stir bar in the bottom of the cell body and insert the cell top with the coiled platinum electrode into the cell. The electrode should be opposite the fritted arm.

3. Add 0.25 cm (enough to cover the bottom) potassium iodide (KI) to the bottom of the side arm (anode compartment) of the cell.

4. Fill the side arm with 10 or more mL of anode solution so as to cover the filter and submerge at least 0.5 cm of the silver anode in solution; the amount of liquid will vary as the anode is consumed (over a period of months) in the analysis.

5. Place the solid silver electrode into the side arm with the silver submerged in the solution.

6. Make sure the glass of the cell is clean and free of grease, fingerprints, water spots, etc., which affect transparency (and thus %T). Wipe/polish with a paper towel or Kim-Wipe, or wash if necessary.

7. Place the assembled cell into the coulometer cell holder. The side arm should extend out the front and against the right wall of the holder, with the platinum electrode and gas inlet tube toward the back of the holder, *out of the light path*.

Set Analysis Parameters. Check these parameters but most should be already set.

8. Rotate the MODE selection thumb wheel to the 1 position which gives the display of units of micrograms (µg) of carbon to 0.1 units.

9. Rotate the TIME SET thumb wheel until the desired analysis time is displayed (generally 4-7 minutes for TIC).

10. Set the RUN/LATCH switch to the RUN position for continuous analysis. LATCH freezes the display at the time set.

11. Set the COUNTS/TIME switch to COUNTS position so that you can watch the counts of carbon on the display.

Operation

12. Make sure coulometer cell current is OFF.

13. Turn ON the main power switch.

14. Set air flow for internal and adjust to 75-100 cc/min.

15. Connect the cell to the cell to the Carbonate Carbon Apparatus using a one-way (check) valve. Only inset the gas tube in the cell when air is flowing, to avoid coulometer cell solution being siphoned back into the KI scrubber.

16. Attach the electrodes to the cell outlet terminals - red to red, black to black.

17. Turn ON coulometer cell current.

18. Allow cell current to titrate the cell solution to its endpoint (solution color becomes blue with %T at 29. If it is lower than 29%, check that the light path is unobstructed and adjust the arrangement of the tube and electrode to correct).

19. (Heater control is broken - do not use.)

You are now ready to begin the analysis.

Analysis Procedure

1. Run a blank sample using an empty sample container. The blank is normally less than 10 µg C in five minutes.

2. Follow the blank by one or more standards (standard $CaCO_3$ is found in a desiccator near the balance). For best precision, material for each analysis should contain 1-3 mg of C. For our standard calcite, this means that you should use about 10-20 mg of standard.

3. Weigh a sample or standard into a clean, dry, tared test tube and attach to apparatus. Sample should contain 1-3 mg of C; adjust the quantity as you begin to see how much carbon tends to be in your samples. Record sample weight in spreadsheet.

4. Pump 5 mL of acid into the reaction tube. RESET the coulometer.

5. When all of the CO_2 is evolved and titrated, (recognized by a stable coulometer display and a %T of 29), record the value in the spreadsheet.

6. Remove the sample tube, pour residue into a waste container, begin next analysis. Wash tubes and rinse in DI water; let dry completely (can use 100 C oven) before reusing.

7. Neutralize the waste acid with soda ash as you go.

8. Run one standard and one duplicate analysis every ten samples (or more if desired).

Calculations

There is a spreadsheet to calculate %TIC (ccoul.xls on the desktop). The calculation is as follows:

%TIC = {(µg C[display value] - per minute µg C[blank value]) / µg sample weight} x 100

Note: the formula subtracts the per minute blank value (blank value/minutes of counting).

For pure calcium carbonate the value should should be 12.00%. (We accept values from 11.75%-12.25%.) Other carbonates will have varying carbon percentages according to the table below.

Mineral	Cation(s)	C	O_3	mw	%C
$CaCO_3$	40.08	12.01	48.00	100.09	12.00%
$MgCO_3$	24.31	12.01	48.00	84.32	14.24%
$(Ca,Mg)CO_3$	64.39	12.01	48.00	184.41	13.03%
$FeCO_3$	55.85	12.01	48.00	115.86	10.37%
$ZnCO_3$	65.38	12.01	48.00	125.39	9.58%
$MnCO_3$	54.94	12.01	48.00	114.95	10.45%

Shut-down (Carbonate Carbon Apparatus)

The Carbonate Carbon Apparatus should be shut down during periods of non-use.

Remove the tube from the cell.
Turn off main power switch.

Note: To prevent residual acid from marring the exterior of the apparatus, keep a sample tube connected to the apparatus when the system is not in use.

Shut-down (Coulometer)

Short periods (during the day)

Before turning off air flow, disconnect inlet gas flow line into the colometer cell. This prevents coulometer solution from being siphoned out of the cell.

Overnight or longer

Turn OFF the cell current and main power supply.

Cell Changing and Clean-up

Note: Solutions should also be replaced when over 100 mg of carbon have been titrated (for 100 mL of cathode solution).

Turn OFF cell current and main power supply.

Unplug electrodes and remove cell from holder. Replace jumper strap between cell current terminals to protect them.

Dispose of the main chamber solution (cathode solution) into the cathode waste solution bottle. Be sure to remove the stir bar first or be prepared to retrieve it from the waste bottle with a magnetic stir bar retriever. Start a new waste bottle (and label correctly) if necessary.

Dispose of the side arm solution (anode solution) and residual KI into the anode waste solution bottle. Start a new waste bottle (and label correctly) if necessary.

Rinse both cell body and the electrodes thoroughly with DI water.

Clean the glass frit in the anode compartment by pulling acetone through the frit with a vacuum.

Rinse and dry all components.

Store cleaned cell in cell holder and return other components to the drawer.

Periodic Mainetenance and Scrubber Changing

Changing Scrubbers

Air Scrubber (40% KOH)

The KOH solution removes CO_2 from the carrier gas, and should be changed once every week during regular use or when the solution becomes thick and foamy. If a fresh KOH solution is foamy, it should be diluted with DI water.

Preparation

Weigh out 40-45 g of KOH and dilute to 100 mL with DI water. Note: Use caution when adding water to KOH as the reaction is exothermic.

Filling

Remove the dispersion tube, bushing and O-ring from the air scrubber assembly.
Place 15-20 mL of KOH solution in the body of the air scrubber.
Replace the dispersion tube, O-ring and bushing. Slide the dispersion tube through the bushing and O-ring so the fritted end is near the bottom of the scrubber.
Hand-tighten the bushing/O-ring seal and place the filled scrubber in its clamp.

Sample Scrubber (50% KI, pH=3)

Preparation

Weight out 50g of KI and dilute to 100 mL with DI water.
Use H2SO4 to acidify to approximately pH = 3.
Fill the fritted sample scrubber with 10-15 mL of the scrubbing solution.
Acid Solution

One can use a variety of acids to react with the carbonates. Originally we used a 2N HClO4 solution but have since switched to using 2N HCl. The procedure for mixing these solutions is given below.

2N HClO4 Dilute 109 mL of 9.2 N HClO4 in 391 mL of DI water.
2N HCl Dilute 172 mL of 37% HCl in 328 mL of DI water

Note: Always add the acid to the water, not the water to the acid.

STANDARD OPERATING PROCEDURE: TOTAL SULFUR (TS)

Purpose and Analysis Overview (after S. Grosshuesch)

The analysis of total sulfur is accomplished by combustion using two furnaces aligned in sequence. A sample is weighed into a ceramic combustion boat and covered with V_2O_5. The boat is pushed inside the first furnace where sample ignition occurs at 1050°C. In the presence of O_2, sulfur is converted to SO_2 and SO. These gas products are carried through to the second furnace, set at 825°C, where they react with a mixture of granular copper oxide and reduced copper filings to ensure that all sulfur is converted to SO_2. The SO_2 is purged into the sulfur coulometer cell, where it is absorbed and titrated.

The coulometer titration cell contains an anode and cathode compartment. The anode compartment contains platinum-detector and -generating electrodes. The cathode compartment contains a single platinum cathode. The anode compartment is filled with a solution containing methanol, pyridine, water, and tetrabutylammonium iodide; the cathode cell compartment contains a phosphoric acid solution. Inert carrier gas (N_2), containing sample sulfur as SO_2 or H_2S, is delivered to the anode cell compartment. Free iodine is electrochemically produced in the anode cell and reacts with the sulfur gas, as illustrated in the following reactions:

Anode reactions: $SO_2 + I_2 + 2H_2O \leftrightarrow H_2SO_4 + 2I^- + 2H^+$

$H_2S + I_2 \leftrightarrow 2H^+ + 2I^- + S0$

$2I^- \leftrightarrow I_2 + 2e^-$

Cathode reaction: $2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$

The decrease in free iodine proportionally decreases the sulfur detector current, automatically activating the titration current and generating I_2 stoichiometrically. Hydrogen gas is produced in the cathode cell at a rate equivalent to that of iodine generation. After the majority of the analyte is titrated, an increase in the detector current and free I_2 occurs, ultimately stopping the titration when the initial iodine concentration is reached. The titration current is continuously monitored, integrated, and used to calculate the quantity of sulfur delivered to the anode cell. The significant advantage associated with the coulometric titration of sulfur is that the current is the titrant and as a result there is no need for generating and applying standard calibration curves. Most sample analyses for total sulfur can be completed within 10 min. Longer analysis times result if the sample contains more than about 3000 µg of sulfur or if sulfur-bearing compounds in the sample resist oxidation. Analysis times for AVS and CRS measurements are highly dependent on the sample type

and reactivity of reduced sulfur compounds present in the sample. (AVS= acid volatile sulfur, CRS= chromium reducible sulfur)

Safety

The following section regards sound laboratory techniques, safety practices, and manners. You are responsible for following these procedures. The chemicals, glassware, and equipment are potentially hazardous. Lab staff must specifically train you before beginning the procedure. Required personal protective gear: gloves and safety glasses must be worn at all times. You must wear closed toe shoes and long pants. If you have long hair, make sure to tie it back. If you are found without any of these required personal safety devices you will relieved of duties. All sample prep work that involves vanadium penoxide should be conducted in a fume hood while wearing a lab coat, goggles, and nitrile gloves.

Anode Solution (30% Pyridine):

Acute and Chronic Effects: **POISON** Irritation to contact area, drowsiness, headache, unconsciousness, anorexia, fatigue, muscle cramps or incoordination, nausea, vomiting, dizziness, diarrhea, sweating, CNS depression, impaired vision, blindness, difficult breathing, cardiac depression, liver and kidney damage, dermatitis.

- Inhalation: Irritant/narcotic
- Skin Absorption: Irritant/sensitizer/narcotic
- Eye Contact: Irritant
- Ingestion: Narcotic/toxic
- Signs and Symptoms of Exposure: Nasal and throat irritation with unpleasant taste in mouth. Diziness, drowsiness, and headaches
- Medical Conditions Aggravated by exposure: Liver, kidney, or central nervous system disorders

Compound Specific PPE: Wear nitrile gloves, safety goggles or face mask, and lab coat when pouring anode solution in calibration cell. While coulometer being used vent coulometer anode half-cell to fume hood.

Storage: Store in tightly closed container, away from heat or flame. Storage area should be well ventilated. Store away from oxidizers, strong acids, and perchlorates.

Disposal: Dispose of by means in compliance with all State, Local, and Federal Regulations

Cathode Solution (Phosphoric Acid):

- Inhalation: Corrosive, causes irritation with coughing, choking and burns of mucous membranes. Symptoms include dizziness, headache, nausea, weakness and

pulmonary edema. Repeated exposure can cause inflammation and ulcerative changes in the mouth and bronchial pneumonia

- Skin Absorption: Corrosive, causes pain or burns. Repeated exposure may cause dermatitis. Studies show that skin adsorption may occur.
- Eye Contact: Eye burns, pain, lacrimation, photophobia from corrosiveness. Injury ranges from irritation to conjunctivitis to blindness, depending on the concentration and duration of exposure.
- Ingestion: Corrosive, causes burns of mucous membranes of the mouth, throat, and esophagus. Symptoms range from inflammation of respiratory distress to death, depending on the concentration and duration of exposure. Symptoms may be immediate or delayed
- Signs and Symptoms of Exposure: Any irritation or burning of the eyes, skin, or respiratory system, or violent gastroenteritis.
- Medical Conditions Aggravated by exposure: Pre-existing skin disease or respiratory disorder.

Compound Specific PPE: Wear nitrile gloves, safety goggles or face mask, and lab coat when pouring anode solution in calibration cell.

Storage: Store in tightly closed container, away from heat or flame. Storage area should be well ventilated. Store away from strong bases.

Disposal: Dispose of by means in compliance with all State, Local, and Federal Regulations

Methanol:

Acute Effects: Hazardous in case of skin contacts: irritant if ingested, inhaled, or if in contact with eyes. Slightly hazardous in case of skin contact (permeator). Severe over-exposure can result in death.

Chronic Effects: Prolonged contact with skin can cause dermatitis or aggravate existing skin problems. Methanol is readily absorbed into the body following inhalation and ingestion. Skin absorption may occur if the skin is broken or exposure is prolonged. Once absorbed, methanol is rapidly distributed to body tissues.

Compound Specific PPE: All sample prep work that involves methanol should be conducted in a fume hood while wearing a lab coat, goggles, and nitrile gloves.

Storage: Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

Small Spill: Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

Large Spill: Flammable and poisonous liquid. Keep away from heat or sources of ignition. Adsorb with dry earth, sand, or other non-combustible material. Call for assistance with disposal.

Disposal: Dispose of by means in compliance with all State, Local, and Federal Regulations

Vanadium Pentoxide:

Acute Effects: Very hazardous in case of ingestion or inhalation. Hazardous in case of skin contact (irritant) or eye contact (irritant). Slightly hazardous in case of skin contact.

Chronic Effects: The substance may be toxic to gastrointestinal tract, upper respiratory tract, and skin. Repeated or prolonged exposure to the substance can produce target organ damage. Repeated exposure to highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

Compound Specific PPE: All sample prep work that involves vanadium penoxide should be conducted in a fume hood while wearing a lab coat, face mask, goggles, and nitrile gloves.

Storage: Store in a tightly closed container. Store in a cool, dry, well-ventilated area way from incompatible substances

Small Spill: Use appropriate tools to put the spilled solid in a convenient waste disposal container.

Large Spill: Poisonous solid. Do not touch spilled material. Prevent entry into sewers, basements, or confined areas. Call for assistance for disposal.

Disposal: Dispose of by means in compliance with all State, Local, and Federal Regulations

Exposure Limits: 0.1 mg/m3 from OSHA (respirable)

Record Keeping

1. Make sure to record the date, number of blanks, number of standards, and number of samples for each batch of samples run in your lab notebook.
2. Make sure to write down what you do at the time you do it. The sulfur coulometer is a bit finicky and writing things down can reduce headaches later.
3. Record any odd results or problems with the sulfur coulometer. If you are unsure of a result or something seems odd, we encourage you to ask questions. We want you to know that mistakes happen, even to those who have years of laboratory experience. The critical requirement is the mistakes be noted and discussed when they happen so corrections or adjustments can be made. It is generally best to start over.
4. All sample mass and sulfur results should be entered into the "Sulfur_Coulometry_Template" to obtain the %Total Sulfur (%TS) for each sample.
    a. It is best to enter the samples while running the instrument to ensure duplicates and standards fall within an acceptable range for each batch of samples.

Reagents Used

Reagents used are dispensed using the original holding container holding containers, squeeze bottles, or stainless steel spatulas. Reagents used as supplied by the manufacturer include anode solution (~30% Pyridine), anode solution (phosphoric acid), and vanadium pentoxide (neat solid). All reagents are pre-made by manufacturer, which requires no reagent preparation by lab technicians.

Equipment List

All necessary equipment is listed in the catalog with the exception of stainless steel spatulas and a squeeze bottles for methanol.

Procedure

Instrument Set-Up

1. Open the left furnace and check on the status of the reduced copper. It should appear shiny and bright. Blackened copper has been consumed. Either replace the copper with fresh reduced copper or reduce the existing copper with the procedure detailed below. Close the furnace.

2. Turn on the left and right furnaces. Resting temperature is 500°C. Heat the furnaces slowly. Increment in 100°C steps to set-point temperatures. The right furnace set-point is 1050°, the left furnace set-point is 825°C.

3. Connect gas lines. Nitrogen (Ultra-High Purity) should be delivered at a pressure of 7-10 psi and then further adjusted to a flow of 100ml/min using the right hand regulator on the front of the combustion furnace. Oxygen (Ultra-High Purity) should be delivered at a pressure of 7-10 psi and further adjusted to a flow of 100 ml/min using the left hand regulator on the front of the combustion furnace. Hold the reset button in for three seconds while adjusting the oxygen flow.

    a. After setting the flow, the instrument will periodically admit oxygen to the combustion tube (you'll hear a clicking sound). Excess oxygen will consume the reduced copper prematurely!

4. Set up the coulometer.

a. Mode selection thumb wheel position: 1 (units in display will be ugS)
b. Time Set thumb wheel: 10 (minutes)
c. Run/Latch switch: RUN
d. Counts/Time: Counts (although it is OK to switch during run to see time elapsed)
e. Cell filling:

Anode (large side) – place a magnetic stir bar in the cell and fill with 50-100 ml of sulfur anode solution, insert the cell top (platinum anode electrode and dual platinum detector electrode), position the electrodes so the anode electrode is closest to the frit. The dual platinum detector electrodes should spaced about the width of a credit card apart from one another.

Cathode (small side) – Fill with 12-20 ml sulfur cathode solution to the same level as the anode solution. Place the platinum cathode in the side arm with the platinum submerged in the solution.

f. Place the assembled cell in the coulometer cell holder.

Note: Mesh-type electrodes should be oriented parallel to the frit

5. Turning On Coulometer
   a. Turn off the coulometer cell current
   b. Turn on the main power switch
   c. Attach the anode and cathodes to the cell outlet terminals (they are color coded)
   d. Plug in the detector electrode
   e. Turn on the coulometer cell current
   f. Allow the cell current to titrate the solution to its endpoint (~6 μ amps)
      i. The anode solution should be a slightly yellow color when the titration reaches its endpoint

Note: At this point, if the coulometer isn't titrating, delicately adjust the electrodes until they begin to titrate.

6. Blank Runs:
   a. Use an empty ceramic boat filled with a small amount vanadium pentoxide (as much as you would put on a regular sample).
   b. Put the ceramic boat with vanadium pentoxide in combustion tube and push into the combustion furnace using the medal sample rod. Close combustion tube as quickly as possible to reduce the loss of combusted sulfur.
   c. Press the reset button on the sulfur coulometer
   d. Wait 10 minutes and record the μg S in the "Sulfur_Coulometry_Template" . Blanks will range from 5 to 40 μg S
7. Sample Runs:

a. Weigh sample out on a clean ceramic boat (50 to 150 mg depending on sulfur content)
b. Cover sample completely with vanadium pentoxide
    i. To reduce the likelihood of spilling vanadium, pre-weigh all the samples you plan to run and place them in order (make sure to write down the order!) in secondary containment.
    ii. Place pre-weighed samples in the fume hood.
    iii. Put a lab coat, nitrile gloves, and lab goggles on before handling vanadium.
    iv. Cover each pre-weighed sample completely with vanadium pentoxide.
    v. Bring the samples back into the coulometry room in the secondary containment
c. Put your first ceramic boat with sample and vanadium pentoxide in combustion tube and push into the combustion furnace using the medal sample rod. Close combustion tube as quickly as possible to reduce the loss of combusted sulfur.
d. Press the reset button on the sulfur coulometer
e. Wait 10 minutes (or until the µg S has changed less than 0.5% in 1 minute) and record the µg S in the "Sulfur_Coulometry_Template" as outlined in the Data Analysis section

8. Standard runs: Precision and evaluation of the instrument set-up is determined by running sodium sulfate standard (Na_2SO4: 22.5% S) or sulfanilamide standard (18.6 % S). Accept results that are ± 5.0% of the expected S value. Weigh 3-7 mg of sodium sulfate and cover completely with vanadium pentoxide. Standards should be prepared in the same manner samples are prepared.
9. **Copper Reduction Method:**
    a. disconnect the Teflon tubing from the combustion tube outlet fitting
    b. furnaces should be at 500ºC
    c. turn off the oxygen flow
    d. fill the scrubber tube with 2-5 ml MeOH
    e. Insert a piece of Teflon tubing through the top piece of the scrubber extending to the bottom of the scrubber
    f. Disconnect the Teflon tubing from both the breech block inlet and the nitrogen gas exit connection.
    g. Use ¼" or 1/8" unions and 1/8" od. Teflon tubing to complete the following connections:
    h. Connect the nitrogen gas line to the top of the scrubber
    i. Connect the exit of the methanol scrubber to the combustion tube outlet fitting
    j. Connect the breech block inlet to a container filled with water
    k. Set the nitrogen flow to 100-150 ml/min on the instrument regulator (7-10 psi on the tank regulator) and allow the N2 to flow through the methanol until the copper is completely reduced.
    l. Add more methanol as need to the scrubber tube
    m. Water will accumulate in the right side of the combustion tube. Blot this away with a Kimwipe.

10. **Troubleshooting**
    a. Low results?
        i. leaks?
        ii. bad sample wt ?
        iii. not enough vanadium pentoxide
        iv. portion of evolved SO_2 missed ? (didn't close combustion tube promptly?)
        v. copper oxide consumed?
        vi. Reduced copper consumed?
    b. High results?
        i. bad sample wt ?
        ii. Takes too long to finish titration?
        iii. One of the electrodes flaky? Try very delicately touching the electrode wires.

Clean Up

1. Pour the used cathode and anode solutions into the appropriate waste container. Make sure the stir bar does not fall into the waste container (this is easily avoided by using a small necked funnel to transfer the anode solution to the waste container).
2. Rinse the cell and caps with water.
3. Pour methanol into the anode cell compartment. Use vacuum to pull the MeOH through the cell frit into the cathode compartment. Rinse with large volumes of DI water.
4. Keep S coulometry cell in dry storage area.
    a. Water left in glass frit will cause cathode solution to discolor during next use. It may be helpful to place S coulometry cell (empty) in a desiccator overnight before the next use.
5. Electrodes should be rinsed with DI water and blotted dry before storage.

Data Analysis

1. Enter your blank µg S reading and time into the "blank" column of the "Sulfur_Coulometry_Template". There will be no weight recorded for your blank.
    a. After you have blank entered into the spreadsheet, it will automatically correct each sample and standard.
2. Enter standard and sample mass, resultant µg S, and sample run time (the sulfur coulometer displays the sample run times) in the coulometer into the "Sulfur_Coulometry_Template".
    a. This spreadsheet will automatically calculate the %TS (equation below demonstrates the calculation the spreadsheet makes for you). Make sure that your

standards and duplicates are within the acceptable range. If standards and duplicates are not within the acceptable range, samples must be run again.

$$\%TC = \frac{sample\ mg\ S - (\frac{mg\ S\ blank}{blank\ time} * sample\ time)}{mass\ sample}$$

Document History and References

Atkin, B. P., Somerfield, C., 1994. The determination of total sulphur in geological materials by coulometric titration. Chem. Geol., 111:131-134.

Wilkins, Bischoff, 2006. Coulometric determination of total sulfur and reduced inorganic sulfur fractions in environmental samples. Talanta 70(4):766-773.

STANDARD OPERATING PROCEDURE: TOTAL CARBON/TOTAL NITROGEN (TC/TN)

Preparation and analysis of MN lake sediments submitted to the LLO for TC/TN analysis

Sample condition –

Samples were received from the LRC freeze-dried and ground (Myrbo) in snap-top plastic containers. Some samples contained visible vegetative material. Some samples contained small pebble sized material. Inhomogeneity may result in greater analytical variability or misleading results.

Preparation –

Samples were mixed with a metal spatula before subsampling. Milligram quantities of sample were packed into tin capsules and weighed on a microbalance. Sample FS-63 Caribou was not stable weight-wise. The entire sample was placed in a 60°C oven for 3 hours and cooled in a desiccator before subsampling.

Instrumentation, Analysis and Quality Assurance –

Acetanilide was used as a calibration standard and as a quality assurance sample. A MN Lake Sediment sample prepared in duplicate and a QA sample were run at least every tenth sample. All QA samples were within ±5% of the known Carbon/Nitrogen weight percent for that material.

Elemental analysis was performed using a Costech 4010 ECS.

Paraphrasing from Costech literature: At the start of an analytical cycle, helium carrier gas was switched to a volume of oxygen. Samples were dropped sequentially into a combustion reactor at 1020°C prior to the arrival of oxygen. The sample and tin capsule reacted with oxygen and combusted at 1700-1800°C. The sample was broken down into elemental components, N_2, CO_2, and H_2O. High performance copper wires at 700°C absorbed excess oxygen not used for sample combustion. The gases flowed through a water trap and then through a gas chromatography (GC) separation column at 35°C. As the gases passed through the GC column, they were separated and detected sequentially by a thermal conductivity detector (TCD). The TCD generated a signal proportional to the amount of element in the sample. Costech EAS software compared the elemental peak to a known standard material (after calibration) and generated a report for each element on a weight basis.

Each sample chromatogram was visually inspected. Manual integration was performed as necessary to use only the area of the element of interest in calculations.

Results were manually transferred to the spreadsheet provided by Amy Myrbo and reported via email.