Wild Rice Sulfate Standard Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan

July 2013

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

Minnesota Pollution Control Agency

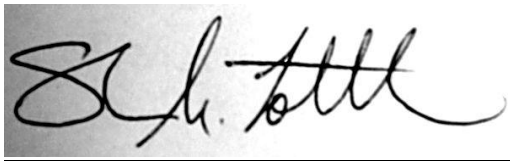
Section A: Project Management Elements

Section A.1: Title and Approvals Sheet

Approval: **Date:**

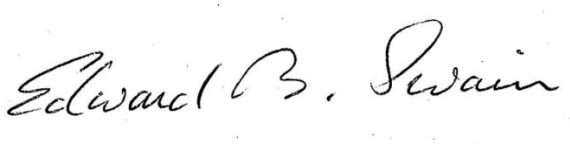
7/28/2013

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



7/31/2013

Shannon Lotthammer
Minnesota Pollution Control Agency
Program Administrator
(651)757-2537
shannon.lotthammer@state.mn.us



7/24/2013

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

Approval: **Date:**

7/24/2013

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

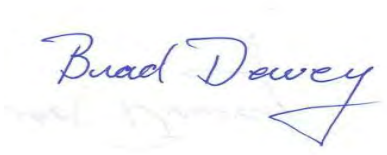
8/1/2013

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

7/30/2013

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

Approval **Date:**



7/28/2013

Brad Dewey
Lab Coordinator
University of Minnesota Duluth
Department of Biology
218-726-7148
bdewey@d.umn.edu

Section A.2: Table of Contents and Tables

Section A.2.1: Table of Contents

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Section A.2.2: Table of Tables

Section A.3: Distribution List

The listed individuals will receive copies of the approved QAPP and subsequent revisions, if applicable:

John Pastor, PhD, University of Minnesota-Duluth, 218-726-7148

Brad Dewey, University of Minnesota – Duluth: Biology, 218-726-7148

Shannon Lotthammer, MPCA, 651-757-2537

Edward Swain, PhD, MPCA, 651-757-2772

Patricia Engelking, MPCA, 651-757-2340

William Scruton, MPCA, 651-757-2710

Paul Moyer, MDH, 651-201-5669

Jeff Brenner, MDH, 651-201-5353

Shane Olund, MDH, 651-201-5357

Section A.4: Project Organization and Responsibility

The Minnesota Pollution Control Agency (MPCA) will conduct project management for the hydroponic experiments with wild rice. The organizational structure of the MPCA is shown in the Minnesota Pollution Control Agency's Quality Management Plan (2013) . The following sections will detail the organization, responsibilities, and lines of communications for each of the personnel involved with the project.

Section A.4.1: The University of Minnesota – Duluth 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 hydroponic study, 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 his discretion, publish results from the project in a peer-reviewed journal.

Section A.4.2: University of Minnesota – Duluth Project Staff

The University of Minnesota – Duluth's project staff will:

- Ensure test procedures are followed.
- Document the test procedure and observations.
- Identify and report any problems to the Principal Investigator.

Section A.4.3: University of Minnesota – Duluth Biology Laboratory Staff

The University of Minnesota - Duluth Biology Laboratory staff will:

- Ensure analytical procedures for the analysis of metals in plant tissue are followed.
- Document the analysis and observations.
- Identify and report analytical problems to the Laboratory Manager

Section A.4.4: MPCA Program Administrator

The Program Administrator will:

- Approve the QAPP including subsequent revisions.
- Provide administrative direction to assigned staff and to the MPCA Quality Assurance/Quality Control (QA/QC) coordinator as needed.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Oversee the preparation of a project summary to include measurable benchmarks, problems encountered regarding QA/QC, and recommended changes in procedures.
- Provide direct supervision and project assignment to assigned staff.

Section A.4.5: The MPCA Project Manager

The MPCA Project Manager will:

- Review and approve the QAPP including subsequent revisions.
- Provide technical 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.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Prepare a project summary to include interpretation of the data, measurable benchmarks, and problems encountered regarding QA/QC, and recommended changes in procedures.
- Review all project deliverables and strategies.
- Provide technical direction for the preparation of work plans and the tasks to be performed.
- Represent the MPCA in meetings.

Section A.4.6: The MPCA Contract Manager

The MPCA Contract Manager will:

- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Review and approve the QAPP including subsequent revisions.
- 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 invoices to ensure proper billing for services provided by the contractor(s).
- Update and distribute the Hydroponics Wild Rice QAPP.
- 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: The MDH Environmental Laboratory Section Manager

The MDH Environmental Section Manager is:

- Responsible for all analytical work performed by MDH.
- Responsible for all MDH Environmental Laboratory section staff and facilities.
- Responsible for the QA function associated with duties performed by the MDH Environmental Laboratory
- Review and approve the QAPP including subsequent revisions.

Section A.4.9: The MDH Environmental Inorganic Laboratory Unit Supervisor

The MDH Inorganic Chemistry Unit Supervisor 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.4.10: 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 MDH Environmental laboratory procedures.
- Review laboratory SOPs.
- Schedule and document pertinent Method Detection Limit studies.
- Maintain staff training records.
- Maintain the laboratory corrective action program.
- Review and approve the laboratory elements of the QAPP.

Section A.4.11: The MDH Laboratory Staff

The MDH Environmental Laboratory staff will:

- Ensure analytical procedures for the analysis of aqueous samples are followed
- Document the analysis and observations.
- Identify and report analytical problems to the Inorganic Chemistry Unit Supervisor.

Section A.5: Definition/Background

Minnesota currently has a water quality standard of ***"10 mg/L sulfate - applicable to water used for 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 standard was adopted into the MPCA water quality standards in 1973 to protect wild rice. Wild rice is an important component of aquatic communities in parts of Minnesota, particularly northern Minnesota. It provides food for waterfowl, and shelter for animals and fish. Wild rice is also a very important cultural resource to many Minnesotans, and is economically important to those who harvest and market wild rice. Based on testimony presented at public hearings leading to the adoption of the sulfate standard, it was intended to apply both to waters with natural wild rice stands and to waters used for paddy rice production.

The MPCA is 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. This QAPP is associated with the part of the overall study that seeks to determine the effects of sulfate exposure on wild rice seed germination and seedling growth via a hydroponic experimental design. The outcomes of this part of the study are listed in Table 1 and Table 2, with target analytes to be quantified in Table 3. The results and interpretation of the outcomes from this specific experiment will be considered in cooperation with the other parts of the overall Wild Rice Sulfate Standard study to inform a decision about the adequacy of the current sulfate water quality standard to protect wild rice.

Section A.6: Project Descriptions

Section A.6.1: Objective

The quality objectives will generally follow the guidance outlined on the MPCA 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. All of the specific values pertaining to precision and accuracy will be refined in the method development phase of the project. These results will be used to amend and modify the values in Table 3 so that the final QAPP reflects specific laboratory derived data quality objectives. This QAPP falls under all requirements of the MPCA's QMP which is approved by U.S. Environmental Protection Agency (EPA) Region 5.

Section A.6.2: Scope

To test how wild rice responds to sulfate, sulfide, and assorted cations and metals, we will grow wild rice seedlings in hydroponic solutions in which the concentrations of sulfur species and cations will be controlled independently. The purpose of these experiments is to provide an experimentally controlled measurement of wild rice growth that can then be compared to observed wild rice distribution in relation to measured pore water concentrations of these chemical parameters in lake sediments. This particular QAPP is concerned solely with the QA/QC activities associated with the section of the experiment that seeks to determine the effects of sulfate exposure on germination and seedlings growth in oxic (oxygen present) conditions.

The hydroponic experiments will be conducted by procedures modified from Li et al. (2009), who examined the responses of cattail (*Typha domingensis*) and sawgrass (*Cladium jamaicense*) to sulfate and sulfide concentrations. All experiments will be conducted in a Percival growth chamber at a photon flux density of 1000 micromol m^{-2} sec^{-1}. Wild rice photosynthesis is thought to reach maximum rates at this photon flux density (Zhao et al. 2004; Sims, Pastor, Dewey, Hildebrandt, unpublished data).

Characteristics of wild rice growth

Wild rice is a native plant of Minnesota and a member of the grass family of plants. Its growth habits are as an annual aquatic plant, which means that its entire life cycle is completed in an aquatic environment. Briefly, each year's new plants come from seeds preserved in the sediment from a previous year's production. The growth of the new plants follows a pattern of seed sprouting, roots that grow into the sediment, and leaves that grow toward the water surface and establish a "floating-leaf" stage where the leaves lay flat along the air/water interface. Additional growth from the root base establishes a "tiller" stage that is quite rigid and grows above the water surface. More than one tiller may develop in each plant. This is the main stem that eventually, after about four months of growth, develops the flowering portion of the plant. The flowers, once fertilized, produce the seed for subsequent generations of the plant.

It is within this context that these toxicity tests will be performed in efforts to better describe effects of sulfate, sulfide, and other parameters on growth and survival of wild rice.

Method Development Objectives

This was an operational guideline used to develop appropriate methods for implementing exposures using wild rice under a hydroponic test strategy. The intent of this test strategy was to investigate the best approach for exposures of wild rice grown in control media and under experimental test conditions using the experimental apparatus anticipated to be used in subsequent toxicity tests. The intended output of these wild rice hydroponic studies is to describe dose-response relationships for two intended toxicants tested separately: sulfate and sulfide. Methods developed will be incorporated into the Appendix of this QAPP.

Table 1: Wild Rice Sulfate Standard Hydroponic Germination Study – Sulfate (Oxic conditions) Measurements

Measurement	Unit	Standard Operating Procedure
Observations of seeds every 2 days	Date, Time, Treatment Level, Replicate Number	Appendix C: Germination Test: Oxic Conditions
Length of Plant Growth – Mesocotyl Growth	Nearest millimeter	Appendix C: Germination Test: Oxic Conditions
Count of Seeds that Germinated	Count	Appendix C: Germination Test: Oxic Conditions

Table 2: Wild Rice Sulfate Standard Hydroponic Juvenile Seedling Study – Sulfate (Oxic conditions) Measurements

Measurement	Unit	StandardOperating Procedure
Observation of Sprouts	Observations and abnormalities noted with date, time, treatment level, and replicate number	Appendix C: Juvenile Seedling Growth Test: Oxic Conditions
Measures of stem/leaf length (mesocotyl growth)	nearest mm	Appendix C: Juvenile Seedling Growth Test: Oxic Conditions
Individual Whole Plant Biomass (dry)	nearest 0.1 mg	Appendix C: Juvenile Seedling Growth Test: Oxic Conditions
Individual Plant Root Area and Length – Scan	Nearest mm^2/mm	Appendix C: Juvenile Seedling Growth Test: Oxic Conditions
Individual Plant Component Weight (Dry)- Roots and Stems/Leaves	nearest 0.1 mg	Appendix C: Juvenile Seedling Growth Test: Oxic Conditions

Table 3: Proposed Project Target Analytes and Chemistry Characteristics in Water to be analyzed by the MDH Inorganic Environmental Laboratory

Target Analyte in Solution	Report Level (mg/L)	Standard Operating Procedures	Analytical Method Reference	Holding Time
Alkalinity, Total	10 mg/L	Appendix B	SM 2320 B	14 Days
Ammonia	0.050 mg/L	Appendix B	EPA 350.1	28 Days
Arsenic	0.00100 mg/L	Appendix B	EPA 200.8	180 Days
Boron	0.0200 mg/L	Appendix B	EPA 200.7	180 Days
Calcium	2.00 mg/L	Appendix B	EPA 200.7	180 Days
Chloride	0.0500 mg/L	Appendix B	EPA 300.1	28 Days
Cobalt	0.00100 mg/L	Appendix B	EPA 200.8	180 Days
Copper	0.0100 mg/L	Appendix B	EPA 200.8	180 Days
Conductivity	0.2 micromhos/cm	Appendix B	EPA 120.1	28 days
Dissolved Organic Carbon	1.00 mg/L	Appendix B	SM 5310 C	28 Days
Iron	5.00 mg/L	Appendix B	EPA 200.8	180 Days
Magnesium	2.00 mg/L	Appendix B	EPA 200.7	180 Days
Manganese	0.0100 mg/L	Appendix B	EPA 200.8	180 Days
Molybdenum	0.00100 mg/L	Appendix B	EPA 200.8	180 Days
Nitrate + Nitrite	0.050 mg/L	Appendix B	EPA 353.2	28 Days
Nitrogen, Total	0.050 mg/L	Appendix B	QuikChem 10-107-04-3-D	28 Days
Phosphorous, Total	0.0100 mg/L	Appendix B	EPA 365.1	28 Days
Potassium	0.500 mg/L	Appendix B	EPA 200.7	180 Days
Selenium	0.00100 mg/L	Appendix B	EPA 200.8	180 Days
Silica, Total Reactive	0.500 mg/L	Appendix B	SM 4500 SiO_2 C	28 Days
Sodium	0.500 mg/L	Appendix B	EPA 200.7	180 Days
Sulfate	0.0500 mg/L	Appendix B and Appendix C	EPA 300.1	28 Days
Sulfide	0.0100 mg/L	Appendix B	QuikChem 10-116-29-3-A and Standard Method 4500-S2– D Equivalent	14 Days
Zinc	0.0100 mg/L	Appendix B	EPA 200.8	180 Days

Table 4: Proposed Target Analytes and Chemistry Characteristics in Water to be analyzed by the U of M Duluth Biology Laboratory

Target Analyte in Solution	Report Level (mg/L)	Standard Operating Procedures	Analytical Method Reference	Holding Time
Sulfate	2.5 mg/L	Appendix C	QuikChem Method 10-116-10-1-A	28 days

Project Schedule Timeline

Method development began in June 2012. Preliminary tests were conducted to determine practicality of test design in preparation for full test implementation. Subsequent tests were performed based on hypotheses to be tested and information observed from test outcomes, as

determined in consultation between the Principal Investigator and the Project Manager. Final experimental procedures were completed in early July, 2013 and the primary wild rice sulfate toxicity experiments, with the goal of producing conclusive and defensible results, are to be conducted at the end of July and beginning of August, 2013.

Section A.6.4: Intended Data Usage

The data is used to determine the effects of sulfate concentration on the growth of wild rice.

Section A.6.5: Technical Reports

The principal investigator will provide a draft report to the MPCA on the wild rice hydroponics method development and research completed by December 2012. The MPCA project manager and wild rice team will review and provide comments to the principal investigator. After revising the report to reflect MPCA comments, the principal investigator will deliver a final report on the hydroponics research completed in 2012 to the MPCA by January 15, 2013. This report will be shared with MPCA management and distributed to interested parties in advance of a mid-project review meeting that will be held on February 28-March 1, 2013. The Principal Investigator will provide a final report on the protocol, results and raw data from the hydroponics research completed in 2012 and early 2013 to the MPCA by March 29, 2013. Upon review, this report will be shared with management at MPCA, MDH, the Wild Rice Standards Study Advisory Committee and other interested parties. Subsequent toxicity testing results and data completed in 2013 will be reported to the MPCA by October 31, 2013.A final report on the results of these experiments, including spreadsheets with pertinent data, will be provided to the MPCA by November 27, 2013. These reports will be distributed to the appropriate managers at the MPCA. The MPCA project team also updates management about project process on a routine basis.

Section A.7: Quality Assurance Objectives and Criteria

Section A.7.1: Overview

Research Directions and Decisions

The construct and need for these hydroponic tests are based on information received as part of a scoping process that included participation by technical professionals with experience in wild rice research, aquatic chemistry, aquatic ecology, and other interests pertinent to these studies to test effects of sulfate on wild rice. A final protocol (*The Sulfate Standard to Protect Wild Rice Study Protocol* found on the MPCA website) was developed as part of this endeavor, which laid out a series of hypotheses used to provide questions to guide the direction of actual and potential scientific research. In this series of hypotheses are elements of test design suited for using water only (hydroponic) test media, which are amenable to controlled manipulations of the test parameters.

Inputs to the Decisions

The project management team (Shannon Lotthammer, Edward Swain and Patricia Engelking) along with the Principal Investigator (John Pastor) will be responsible for final decisions on the project. These decisions will be informed by results of the hydroponics tests, scientific technical expertise, outputs from other investigations associated with this study such as the field studies, comments from the Wild Rice Standards Study Advisory Committee, and other sources of technical information.

Laboratory Analysis

The Minnesota Department of Health's (MDH) Environmental Laboratory will provide the majority of the analytical testing for the project. The analytes of concern from an aqueous medium (with Report levels and analytical methodologies) are detailed in Table 1. The MDH Environmental Laboratory's Quality Assurance Manual (QAM) appears in Appendix A while their Standard Operating Procedures appear in Appendix B. The MDH QC acceptance criteria are listed in Table 7. The University of Minnesota Duluth Biology Laboratory will run analyses on sulfate concentrations to be cross checked for accuracy by the MDH. University of Minnesota Duluth Biology Laboratory SOPs are listed in Appendix C.

Section A.7.2: Blanks

The samplers will use field blanks while sampling. Field blanks are submitted at a 5 percent 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 percent) 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 samplers. 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 50 percent.

Section A.7.4: 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. MPCA policy allows a maximum recovery of 150 percent and a minimum recovery of 30 percent. The laboratory uses Municipal Section (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 percent rate of spikes.

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

Section A.7.6.1: Precision

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:

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

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

Section A.7.6.2: 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 spiked 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 (unspiked) sample concentration. The formula for determining percent recovery is as follows:

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

Acceptable data falls between 30 percent and 150 percent recovery.

Section A.7.6.3: 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.7.6.4: 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.7.6.5: 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:

$$\%\ \text{Complete} = \frac{\text{(\# of Valid Results) * 100}}{\text{(\# of Samples Tested)}}$$

A completeness of 90 percent 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 percent completeness, the data are rejected. If the laboratory is at fault, they will be responsible for securing the re-collection and re-analysis of samples.

Section A.8: Specialized Training/Certifications

University of Minnesota, Duluth (UMD Department of Biology) lab personnel have been trained for proper sample handling, preparation, and analytical techniques and safety. 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 by UMD.

The Minnesota Department of Health Environmental Laboratory personnel have been trained for proper sample handling, preparation, and analytical techniques and safety. 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 by the Laboratory's Quality Assurance Office.

Section A.9: Record Keeping

The water samples collected will be documented using established tracking methods of the Pastor lab.

- All records will be kept in the laboratory.
- All data will be entered for statistical analysis in Excel spreadsheets.
- The lab coordinator for the Principal Investigator will oversee data entry and proof checking.
- All data files will be sent to the MPCA project managers and coordinator.
- The effect of sulfate levels on wild rice seed, shoot, and root growth will be tested using a randomized complete block analysis of variance.

The approved QAPP will be recorded and submitted those indicated on the distribution list. The records are retained for a period of not less than five years.

Section B: Data Generation and Acquisition

Section B.1: Sampling Design

This section describes the methods used for conducting toxicity tests using various wild rice growth endpoints to examine effects of sulfate under oxic (aerobic) conditions. Toxicity tests use a hydroponic (aqueous) exposure media to deliver selected concentrations of sulfate that provide the conditions adequate for the normal growth of the wild rice test organism. Wild rice in two different stages of growth is used for initiating the experiments either as a germinating seed (Germination Test) or as seeds that have sprouted (Juvenile growth test). Specific details of each test design are provided in the methods titled: 1) ”Germination Growth Test: Oxic Conditions”, and 2) “Juvenile Seedling Growth Test: Oxic Conditions” found in Appendix C.

Section B.2: Sampling Methods

Parameters of plant growth to be measured

This section describes the procedures of obtaining samples and performing specific measurements of plant growth as described in the methods titled: 1) ”Germination Growth Test: Oxic Conditions”, and 2) “Juvenile Seedling Growth Test: Oxic Conditions” found in Appendix C.

Plant sampling

Following the 10 day experimental period plants will be measured for total length and total weight (biomass) as described in the methods titled: 1) ”Germination Growth Test: Oxic Conditions”, and 2) “Juvenile Seedling Growth Test: Oxic Conditions” found in Appendix C. The methods used for obtaining these physical measurements are cited in the test methods.

Growth media sampling

The toxicity tests described in the methods titled: 1) ”Germination Growth Test: Oxic Conditions”, and 2) “Juvenile Seedling Growth Test: Oxic Conditions” found in Appendix C require the exposure solutions to be renewed every two days. Both the new solutions and 2 day old solutions are sampled for analysis of water chemistry. The procedure for sampling and methods used for chemical analysis are cited in the test methods (Appendix C)

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This section describes the procedures of obtaining samples and performing specific measurements of plant growth as described in the methods titled: 1) "Germination Growth Test: Oxic Conditions", and 2) "Juvenile Seedling Growth Test: Oxic Conditions" found in Appendix C.

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The toxicity tests described in the methods titled: 1) "Germination Growth Test: Oxic Conditions", and 2) "Juvenile Seedling Growth Test: Oxic Conditions" found in Appendix C require the exposure solutions to be renewed every two days. Both the new solutions and (2 d) old solutions are sampled for analysis of water chemistry. The procedure for sampling and methods used for chemical analysis are cited in the test methods (Appendix C)

Analytical Endpoints: Both Experiments

For both germination and seedling experiments newly made test solution and old test solutions used throughout the experiment are stored in labeled bottles for analysis of various compounds listed in Table 3. The analytical procedures used in the analyses of these various chemical parameters are provided through the MDH inorganic environmental laboratory SOPs located in Appendix B of this QAPP. Analytical holding times, preservation methods, and volumes required for each analyte are listed below in Table 5. They are also listed in the U of M Duluth Biology Laboratory Analytical SOPs (Appendix C) and MDH analytical SOPs (Appendix B).

Table 5: Sulfate Concentration Endpoints

Analyte/Endpoint	Minimum Volume Needed	Holding Time	Preservation Method
New Test Solutions – Sulfate	5 ml	Stored for a maximum of 25 days	Stored at 4 ºC
Old Test Solutions – Sulfate	5 ml	Stored for a maximum of 25 days	Stored at 4 ºC

All corrective actions taken during the experimental processes are documented by Dr. John Pastor and Brad Dewey of the University Of Minnesota-Duluth Biology Department, and appropriate MPCA personnel are notified. All corrective actions in analyte analysis conducted at the MDH are documented by Jeff Brenner and appropriate MPCA personnel are notified.

Section B.3: Sample Handling and Custody

All samples collected will be labeled to identify the sample for the database record. The labels will include location, data, time, and other information documents as required. Sample labels must be properly completed to include the sample's identification number. Labels shall be printed and affixed to the outside wall of the sample container in the lab, prior to going to the field.

All laboratory-identified samples will be labeled for the database record. The labels will include the abbreviation of date, method, location, size, and media.

The MDH Inorganic Environmental Laboratory QA Manual – Appendix 4, 5, and 6 and Sample Receiving Procedure Manual outline the procedures for custody within the laboratory. These manuals are found in Appendix A of this QAPP.

Section B.4: Analytical Methods

Information on the analytical methods to be employed by the Minnesota Department of Health is detailed in Table 3. University of Minnesota - Duluth - Biology Department analytical methods are available in Appendix C of this QAPP.

Section B.5: Quality Control

Field and laboratory QC checks are identified in Table 6. The frequency of analysis and the control limits are also listed. If the results do not meet the QC acceptance criteria, corrective actions are defined. Table 7 lists the quality control acceptance criteria for the aqueous analytical chemistry conducted by the MDH Inorganic Environmental Laboratory. A description of Dr. John Pastor's Lab and the U of M - Duluth's Biology Lab quality control activities are described in this section below and in Table 8.

Table 6: Quality Control Elements require by all laboratories performing analytical work for this study

QC Type	Water
Blanks	
Laboratory Blanks	1 per analytical batch*
Method Blanks	1 per analytical batch
Spikes	
Matrix Spike	1 per analytical batch
Laboratory Control Sample	1 per analytical batch
Surrogates (as appropriate)	1 per analytical batch
Calibration Checks	1 per analytical batch
Duplicates	
Matrix Spike Duplicates	1 per analytical batch
Laboratory Duplicates	1 per analytical batch

*An analytical batch is considered to be no more than 20 samples, not including the QC elements

Table 7: Aqueous Quality Control Acceptance Criteria

Target Analyte	Matrix Spike (% Recovery)	Laboratory Control Spike (% Recovery)	Relative Per Cent Difference (%)
Alkalinity, Total	90-110	90-110	15
Ammonia	90-110	90-110	10
Arsenic	85-115	85-115	20
Boron	85-115	85-115	20
Calcium	85-115	85-115	20
Chloride	90-110	90-110	10
Cobalt	85-115	85-115	20
Copper	85-115	85-115	20
Dissolved Organic Carbon	90-110	90-110	10
Iron	85-115	85-115	20
Magnesium	85-115	85-115	20
Manganese	85-115	85-115	20

Molybdenum	85-115	85-115	20
Nitrate + Nitrite	90-110	90-110	10
Nitrogen, Total	90-110	90-110	10
Phosphorous, Total	90-110	90-110	10
Potassium	85-115	85-115	20
Selenium	85-115	85-115	20
Silica, Total Reactive	90-110	90-110	10
Sodium	85-115	85-115	20
Sulfate	90-110	90-110	10
Sulfide	80-120	90-110	10
Zinc	85-115	85-115	20

Dr. John Pastor's Laboratory Quality Control Elements

Germination Growth Test: Oxic Conditions Acceptability of Test Results

1. At least 90% of germinated seeds in control jars are living at test termination.
2. Seed are considered germinated when mesocotyl length from control exposures will be at least 2.0 cm at the end of the 10 days duration of growth.
3. Control germinated seeds should not indicate any visible phytotoxic or developmental symptoms at any time during the test.

Juvenile Seedling Growth Test: Oxic Conditions Acceptability of Test Results

1. At least 90% of control juvenile seedlings are living at test termination
2. Mesocotyl length of living juvenile seedlings from control exposures will be at least 5.0 cm at the end of the 10 d duration of growth.
3. Control juvenile seedlings should not indicate any visible phytotoxic or developmental symptoms at any time during the test.

Plant Biomass QA Control Acceptance Criteria: Germination and Juvenile Seedling Growth Test

1. Determination of stable dry weight is achieved by placing three individual weighing pans plus plant material into the desiccator jar. Once cooled, the weight of each pan is recorded, and the pans are placed back into the drying oven for one half hour. After this, the pans are removed, placed into the desiccator jar to cool and weighed once again. If the dry weight of each pan differs by less than 0.5 mg or 4%, whichever is less, the weight is stable and the weighing of all individual weighing pans with plant matter can be completed.

Area and Length QA Acceptance Criteria: Germination and Juvenile Seedling Growth Test using the Epson Perfection 4990 photo scanner controlled by the image acquisition component of Regent Instruments,

WinFOLIA software

1. The root image is observed and accepted or determined to be not acceptable (roots extending outside of scanned area, fuzzy image due to roots "drifting", air bubbles along root surface)
2. Roots are scanned until an acceptable image is produced

U of M Duluth Biology Quality Control Acceptance Criteria

The University of Minnesota- Duluth's Biology Laboratory, managed by Brad Dewey, will conduct sulfate analysis on new renewal solutions and old renewal solutions via a Lachat Quik Chem 8000 flow injection autoanalyzer (QuikChem Method 10-116-10-1-A, Determination of Sulfate by Flow Injection). The quality control elements for this analysis are listed in Table 6. Quality control acceptance criteria are listed below in Table 8. All values are based upon the current laboratory acceptance criteria and shall not exceed these values, otherwise the system will be deemed to be out of control and corrective actions will need to be taken before the analytical batch is reanalyzed.

Table 8: UMD Biology Lab Quality Control Acceptance Criteria

Target Analyte	Matrix Spike (% Recovery)	Laboratory Control Spike (% Recovery)	Relative Per Cent Difference (%)
Sulfate	80-120	80-120	30

Section B.5.1: QC Type

Section B.5.1.1: Method Blanks

One method blank is extracted and analyzed with each batch of up to 20 samples to demonstrate that there are no interferences from the glassware, reagents, and analytical system. If any method blank shows target analytes above ½ the report level, a solvent blank should be injected 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-extracted and re-analyzed.

Section B.5.1.2: Matrix Spikes and Duplicates (MSs/MSD)

Matrix spikes are used to determine if there are any effects related to the sample matrix. One spike should be spiked, extracted, and analyzed per batch of up to 20 samples. A matrix spike duplicate should also be analyzed once per batch of up to 20 samples. The percent recoveries of the MS are used to measure accuracy of the analysis. The percent recoveries should be 30-150 percent.

Section B.5.1.3: Laboratory Control Sample and Duplicate(LCS/LCSD)

A laboratory control sample (LCS) is an aliquot of clean 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 percent 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 percent recoveries should be 30-150 percent for all matrices.

Section B.5.1.4: Laboratory Duplicates

Laboratory duplicates are used to measure precision. One pair should be extracted and analyzed per twenty samples or less. The relative percent difference (RPD) should be ≤50 percent for acceptability of results.

Section B.5.1.5: Out-of-Control Situations

When the out-of-control situations listed in Sections B.5.1.1 through B.5.1.4 occur, the failing analysis should be re-injected into the analytical system. If the re-analysis meets QC criteria, report the second analysis. If the re-injection still does not meet criteria, the affected samples should be re-extracted 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 laboratory. The laboratory staff performs preventative maintenance on a routine schedule on all field equipment. Standardized field sampling equipment (bailers, scoops, bowls, push probes, etc.) 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. Additionally, the laboratory's standard operating procedures (SOPs) present the specific protocols to be followed as part of the analysis. The preventative maintenance plan employed by the laboratory is described in the laboratory QAM. 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 laboratory instruments to be used for the Hydroponics Wild Rice Project for Effects of Sulfate in oxic conditions. 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: Laboratory Procedures

The frequency and procedures used to calibrate equipment including incubators, shakers, water baths, spectrophotometers, pipettes and lasers are described in the manufacturing instructions and/or dictated by the University of Minnesota laboratory Standard Operating Procedure (Appendix C). The calibration procedures followed by the laboratory are outlined in the Laboratory QAMs and SOPs.

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

Standard procedure for inspection/acceptance requirements for supplies will be routinely performed by trained technical personnel in John Pastor's laboratory. The 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.

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.

Section B.9: Non-direct Measurements

Historical data may be used to initiate an investigation. However, all decisions are based on data collected during the project.

Section B.10: Data Management

The samples will be recorded as they are collected. The water samples collected will be documented using established tracking methods of the Pastor lab. All records will be kept in the laboratory. All data will be entered for statistical analysis in Excel spreadsheets. The UMD lab coordinator for J. Pastor will oversee data entry and proof checking. Internally, the MPCA will store all analytical data in their own database.

Section B.10.1: Data Transmittal

Data and laboratory experiment 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. A report of Project activities is prepared by the Program Manager.

Section B.10.2: Data Rejection

Analytical data that does not meet the established QA/QC criteria defined in this QAPP is rejected. Data is evaluated by the technical staff to ensure that it is compliant with the QAPP. Data collected that is judged to be out of compliance are qualified, rejected, or re-collected if possible.

Section B.10.3: Data Tracking

MPCA staff will contact the Principal Investigator on a regular basis regarding the status of project work.

Section B.10.4: 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

A field audit is not scheduled for the project.

Section C.1.2: Laboratory Audits

Section C.1.2.1: Internal Audits

The laboratory QA staff conducts internal audits of all departments involved with the handling/analysis of the project samples. These 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 its operations before data are affected. All audits are documented. If problems occur or corrective action is initiated, the Quality Assurance Coordinator 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.

Section C.1.2.2: External Audits

If external audits of the laboratories are performed, 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.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 is found to be out of control, Corrective Action (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 laboratory 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 project manager (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 laboratory project record. 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. 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 MDH Inorganic Environmental 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 (if applicable),
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 MDH QAM found in Appendix A.

Section C.2.4: Reports to Management

The Principal Investigator will provide a draft report to the MPCA on the wild rice hydroponics method development and research completed by December 2012. The MPCA project manager and wild rice team will review and provide comments to the principal investigator. After revising the report to reflect MPCA comments, the principal investigator will deliver a final report on the hydroponics research completed in 2012 to the MPCA by January 15, 2013. This report will be shared with MPCA management and distributed to interested parties in advance of a mid-project review meeting that will be held on February 28-March 1, 2013. A final report on the protocol, results and raw data from the hydroponics research completed in 2012 and early 2013 will be given to the MPCA by March 29, 2013. After review, this report will be shared with management at MPCA, MDH, the Wild Rice Standards Study Advisory Committee and other interested parties.

Subsequent toxicity testing results and data completed in 2013 will be reported to the MPCA by October 31, 2013. A final report on the protocols and results of these experiments, including spreadsheets with pertinent data, will be delivered to the MPCA by November 27, 2013.

These reports will be distributed to the appropriate managers at the MPCA. The MPCA project team also updates management about project process on a routine basis.

Section D: Data Validation and Usability

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

Section D.1.1: Data Reduction

All data will be entered for statistical analysis in Excel spreadsheets. The UMD lab coordinator will oversee data entry and proof checking. The effect of sulfate levels on wild rice seed, shoot, and root growth will be tested using a randomized complete block analysis of variance. Photographs will also be taken periodically during the growing season to visually document growth and condition of the stems and overall experimental design.

Section D.1.2: Data Verification/Methods

The laboratory manager or designated experienced chemist verifies data is correct as reported. A manager reviews 100 percent 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 a laboratory are described in that laboratory's QAM. The laboratory stores all raw data in their archives for five years. Raw data is available to MPCA staff as needed.

Appendix A: MDH Environmental Laboratory - QA Manual

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

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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.

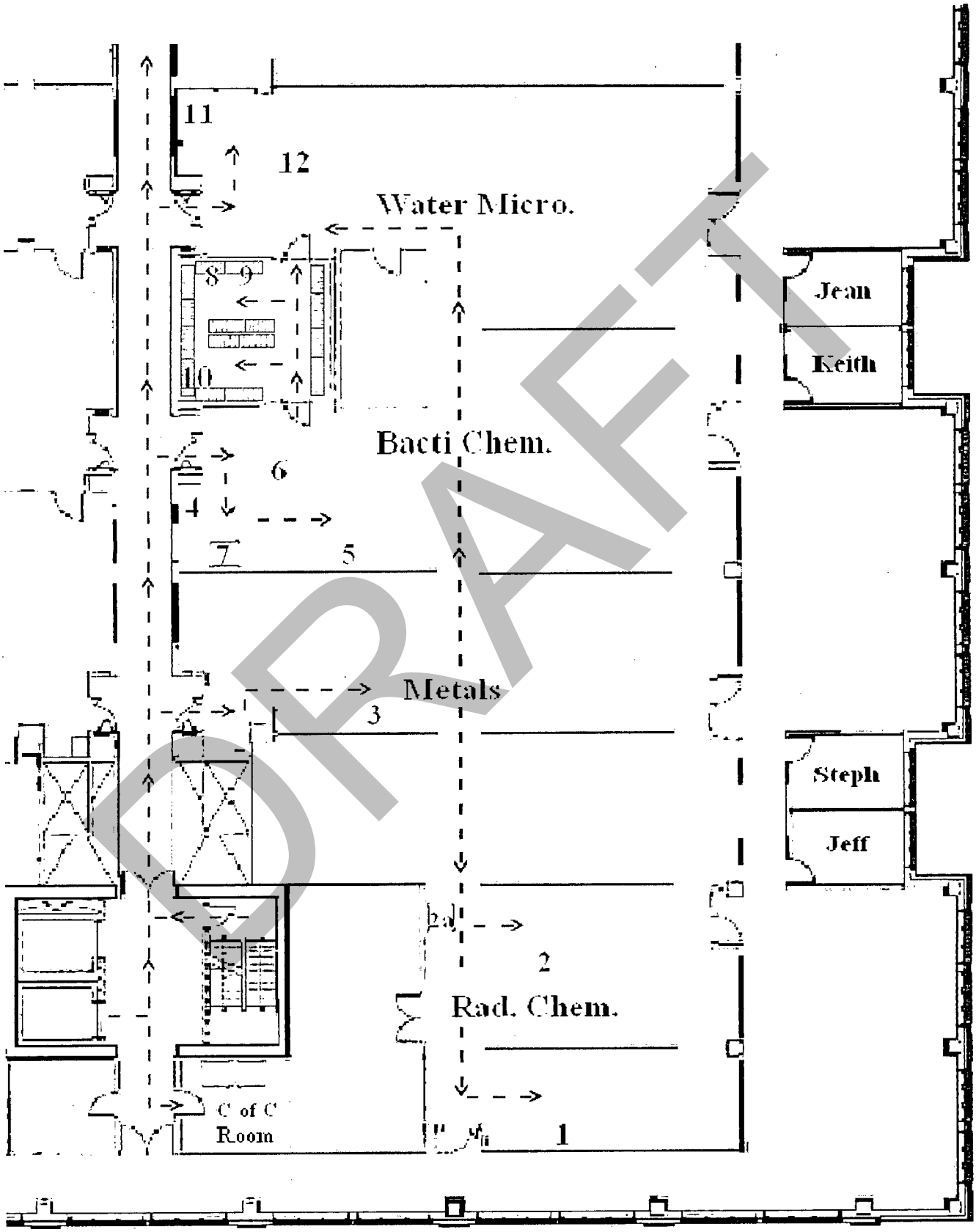
Refer to the **Labs Map, North** for the following sample delivery locations.

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.

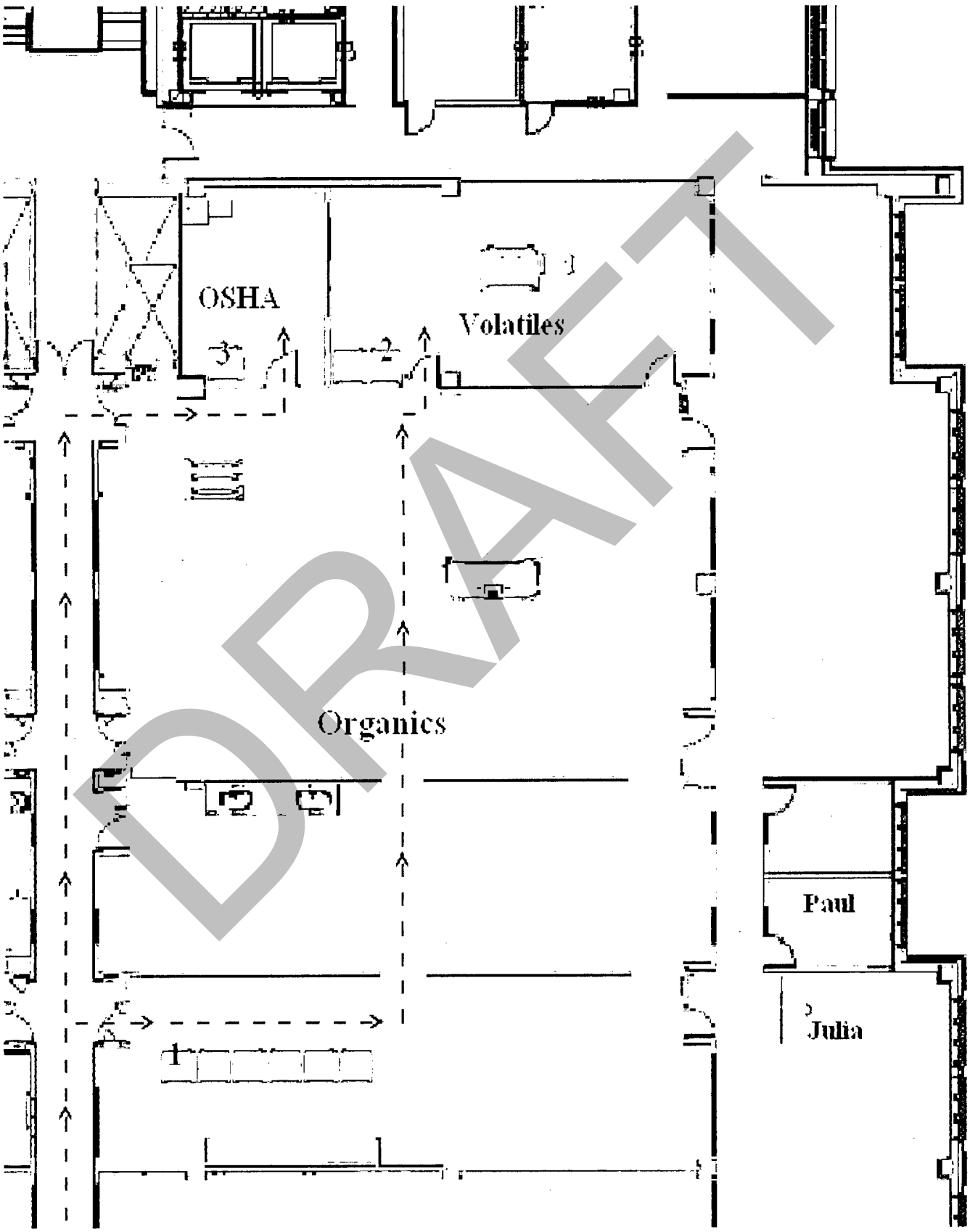
2. ***All volatile organics*** samples go in this fridge. The top two shelves are for 468 VOCs, the lower shelves are for 498 VOCs. Lab sheet copies go in the basket just opposite the cooler.

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

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

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

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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

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Appendices

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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.

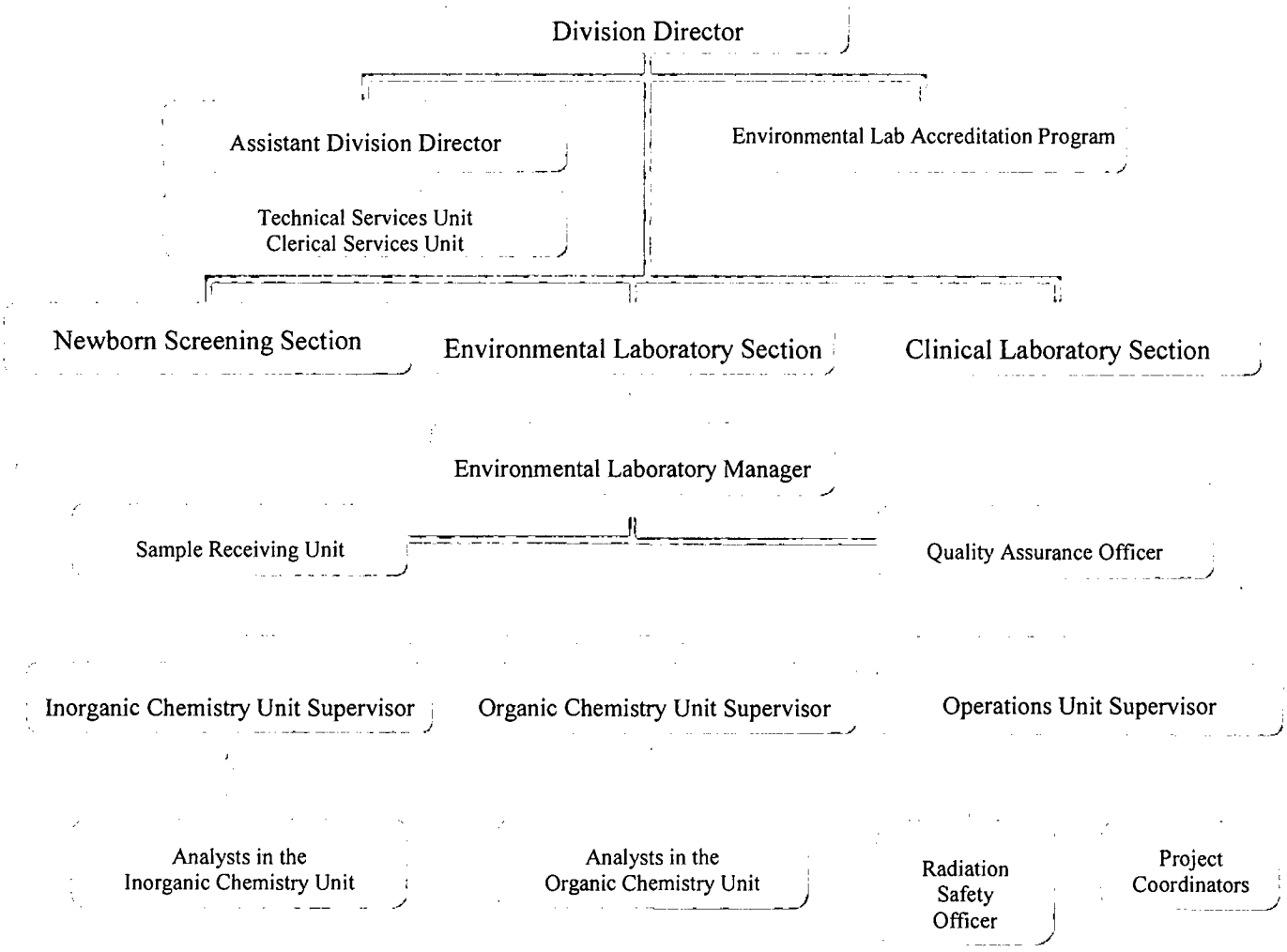
Minnesota Department of Health Environmental Laboratory Sample Receiving Procedure Manual, Rev. 4, Laboratory Information Management Systems and Technical Services Section (2006).

"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, KB = 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	Cyl Level Y/N
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

Appendix B: MDH Environmental Inorganic Laboratory - Standard Operating Procedures

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 2^{nd} 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 <u>essential</u> 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.

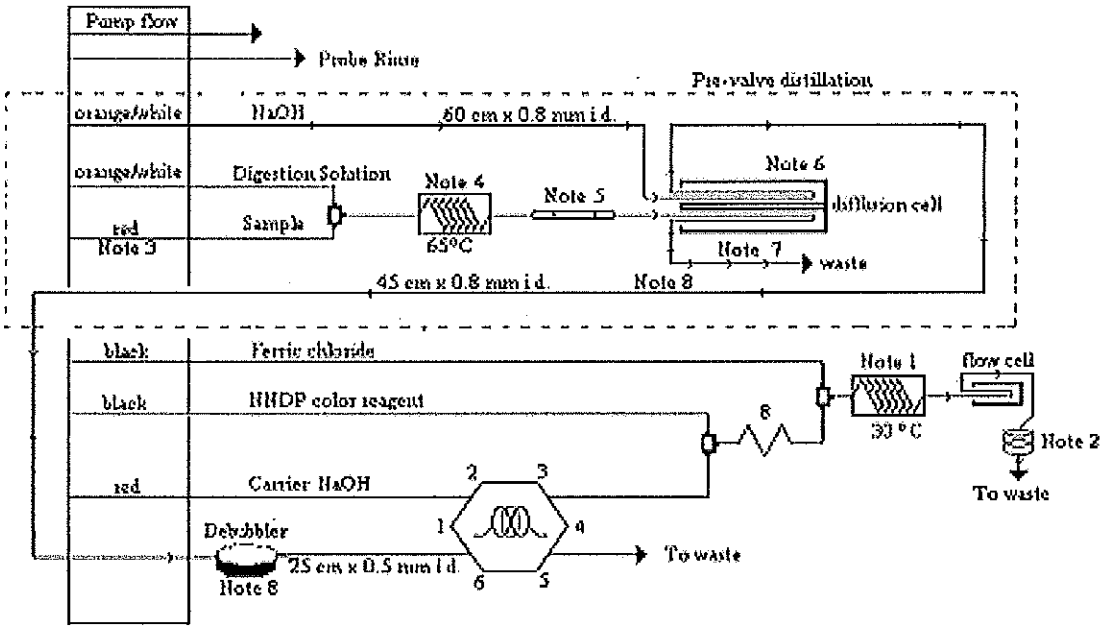
16.2 Lachat Instruments QuikChem® Method 10-116-29-3-A, Determination of Dissolved Sulfide by Flow Injection Analysis.

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 an other 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

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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

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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.

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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.

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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.

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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:

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.

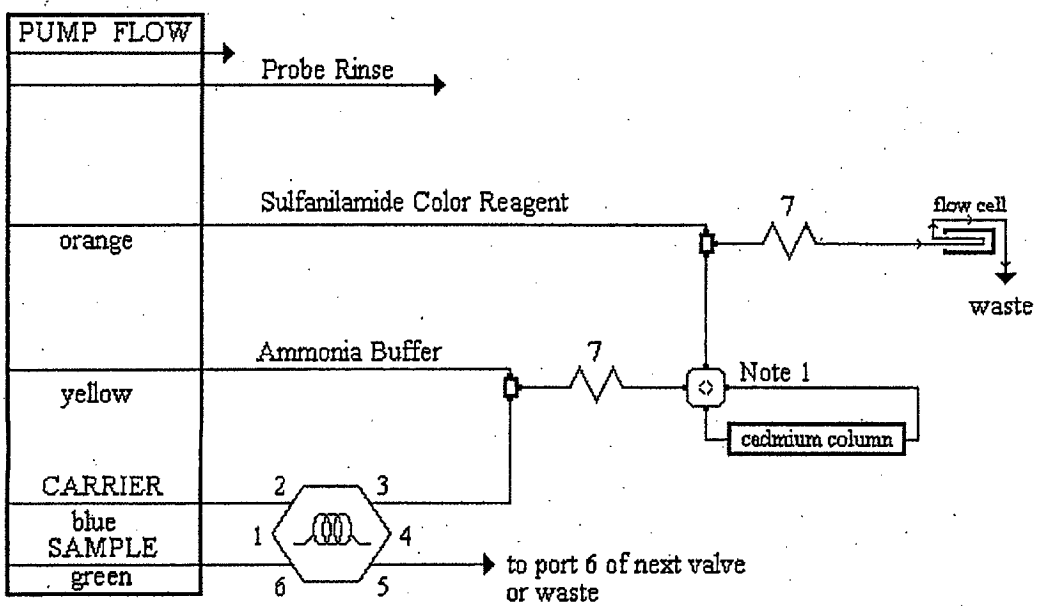
16.4 QuikChem Methods Manual. QuikChem Method Number Method 10-107-04-1-O. Revision date: 18 December 2000.

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:

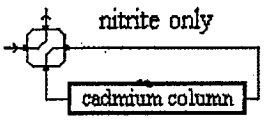


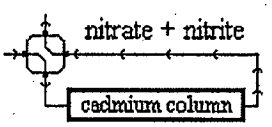
Carrier: **Helium degassed DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000 Sample Loop: 15 cm of **0.5 mm (0.022 in) i.d.** tubing. This is **2.5 µL/cm.**
Interference Filter: 520 nm

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

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.

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[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.

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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.

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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:

Mass	Element	Det. Mode	Integration per point	Time 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: 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

[signature] Date: 04/16/04
(QA Officer)

Procedure Approved By: Jean Kahlainen (Program Manager) Date: 4/19/04

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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.

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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

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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: Will 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:

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.

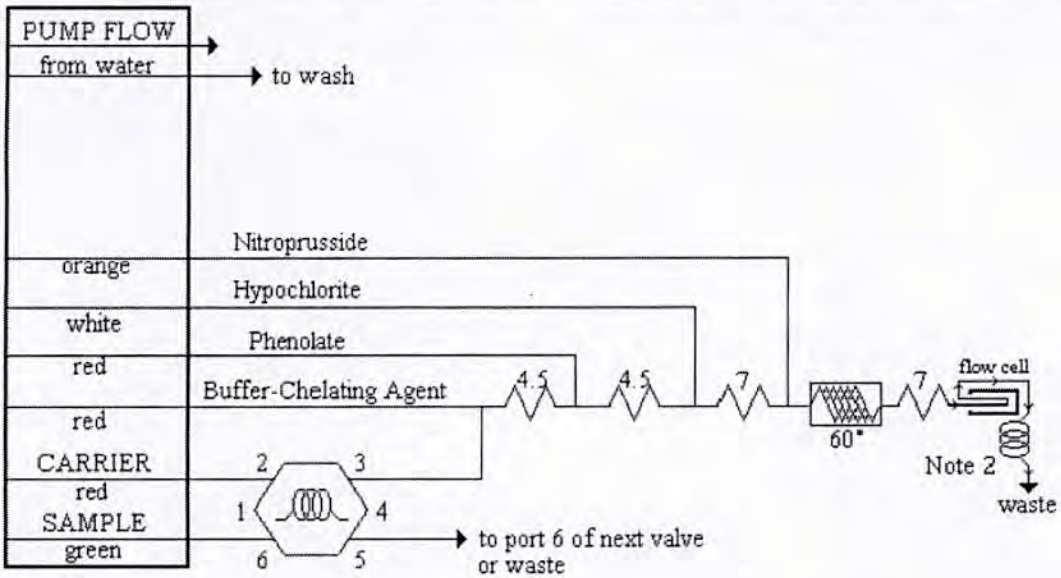
16.3 "Appendix B to Part 136-Definition and Procedure for the Determination of Method Detection Limit-Revision 1.11," Federal Register, Vol 49, No. 209, Friday October 26, 1984, pp. 198-204.

16.4 Lachat Instruments QuikChem® Method 10-107-06-1-C, Determination of Ammonia in Waters by Flow Injection Analysis Colorimetry.

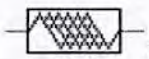
17.0 TABLES, FIGURES, VALIDATION DATA

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

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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

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

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

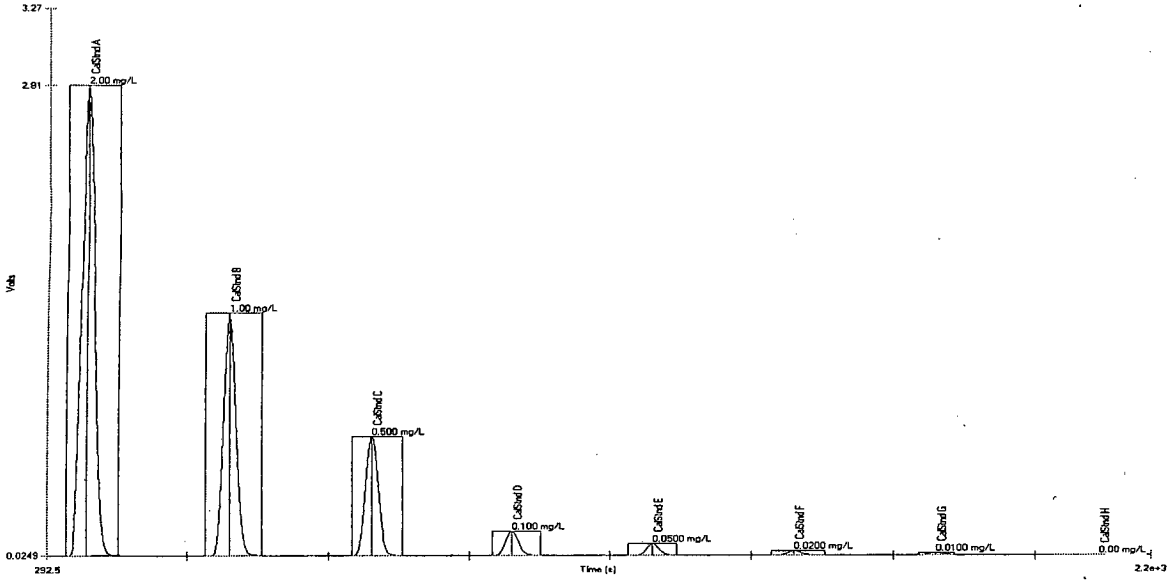
Valve Timing:

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



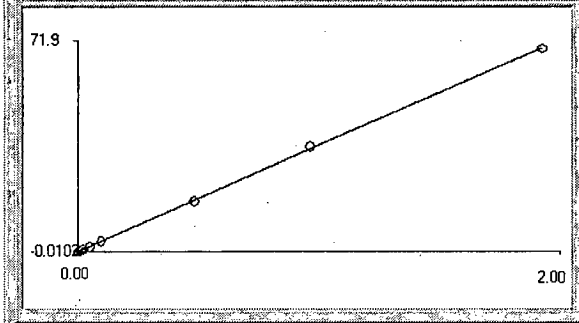
File Name: OM_10-3-2007_01-51-03PM_OMN
Acq. Time: 3 October 2007

Calibration Graph and Statistics

Calibration Results - Channel 1

Sulfide

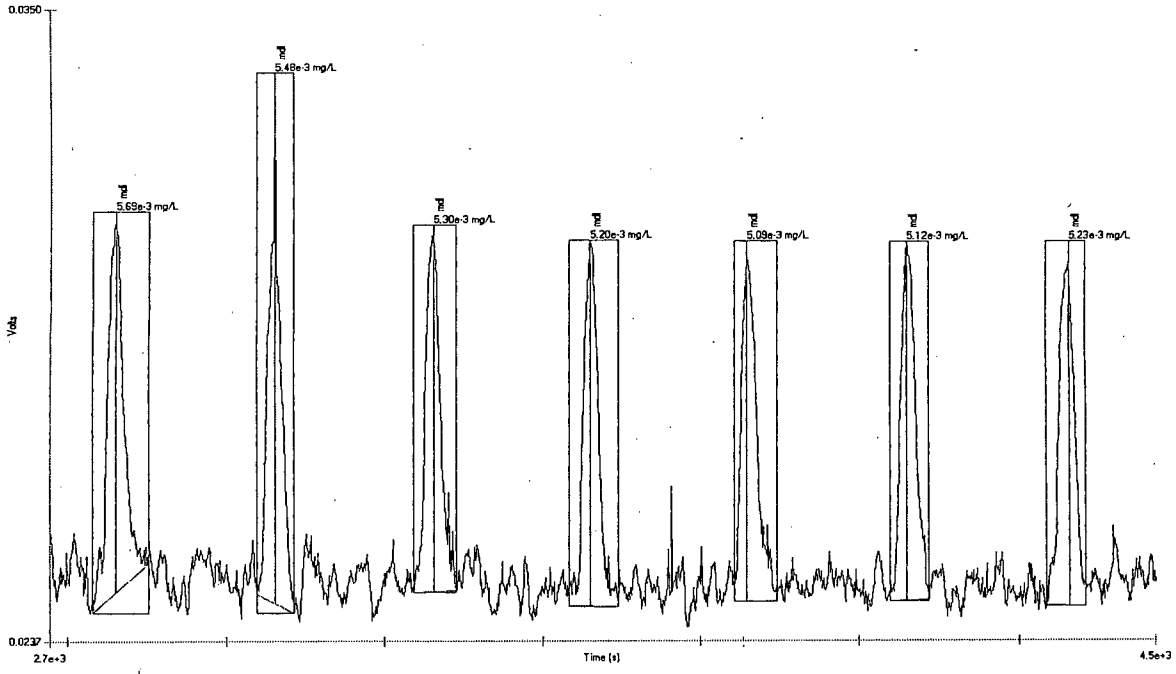
	Known Concentration (mg/L)	Rep	Area (V·s)	Height (V)	% RSD	% Residual	Unused	Det. Conc (mg/L)	Date	Time
1	2.00	1	71.9	2.79	0.0	0.3	☐	1.99	10/3/2007	1:55:53 PM
2	1.00	1	37.0	1.44	0.0	-1.7	☐	1.02	10/3/2007	2:00:01 PM
3	0.500	1	18.0	0.705	0.0	1.5	☐	0.492	10/3/2007	2:04:09 PM
4	0.100	1	3.60	0.141	0.0	1.2	☐	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



Area = - 0.338 * Conc^2 + 36.8 * Conc - 0.0315
Conc = 7.11e-6 * Area^2 + 0.0272 * Area + 8.61e-4
Correlation Coefficient (r) = 1.00000

1/x weighting

Settings



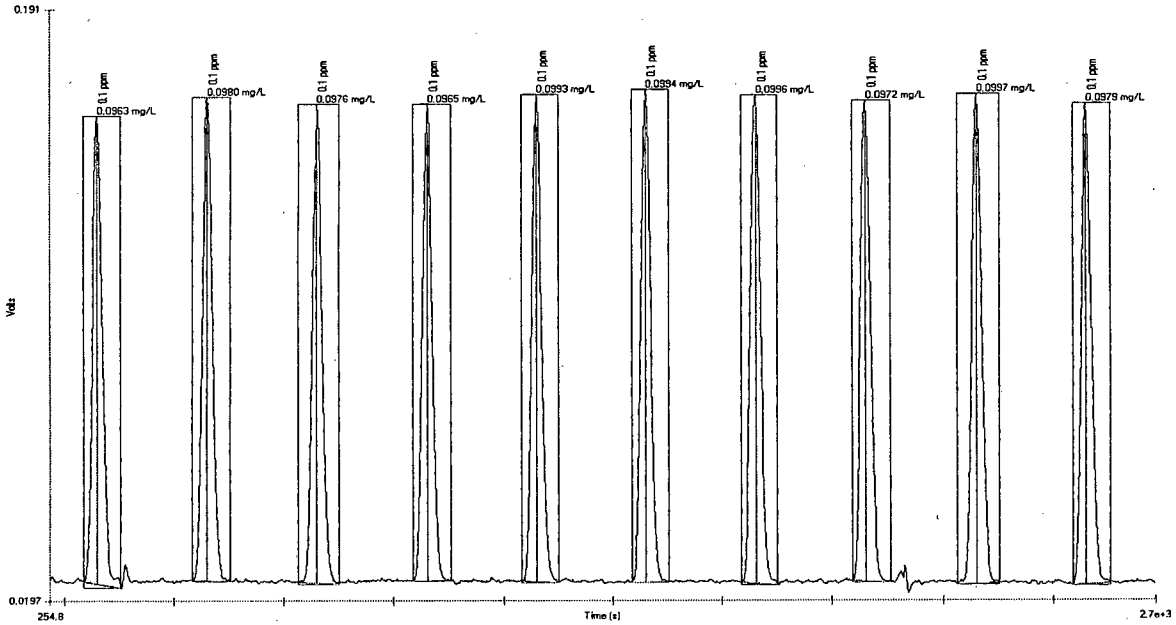
Method Detection Limit for sulfide using a 0.005 mg S/L standard

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



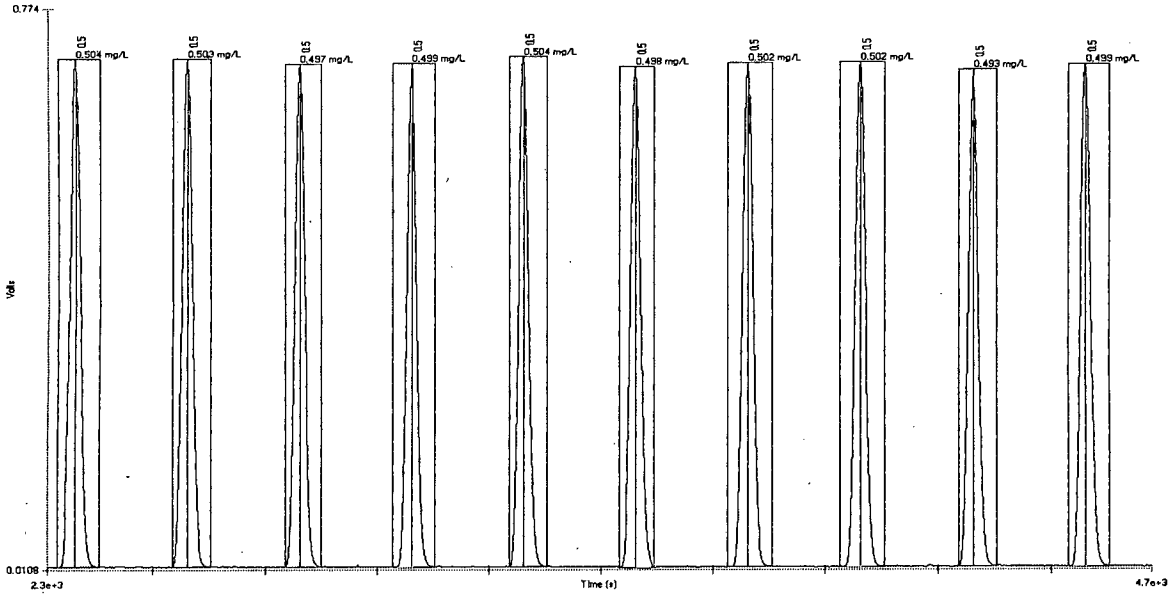
Precision Data for sulfide using a 0.1 mg S/L standard

% 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



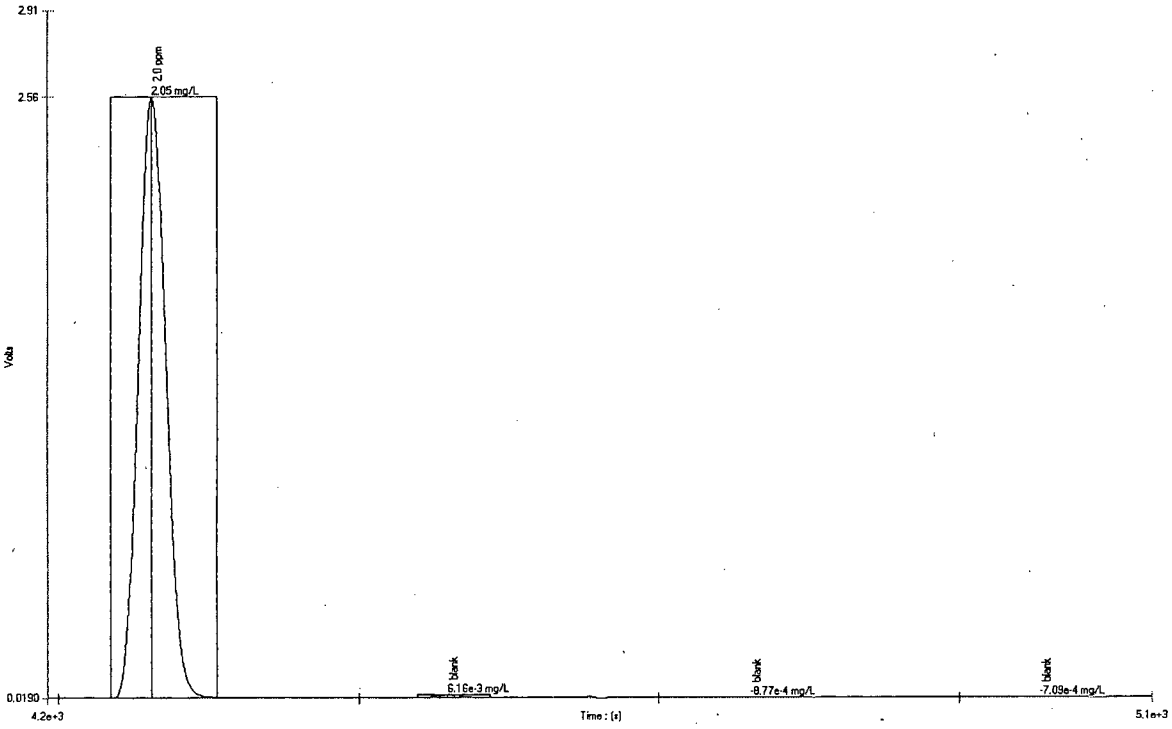
Precision Data for sulfide using a 0.5 mg S/L standard

% 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

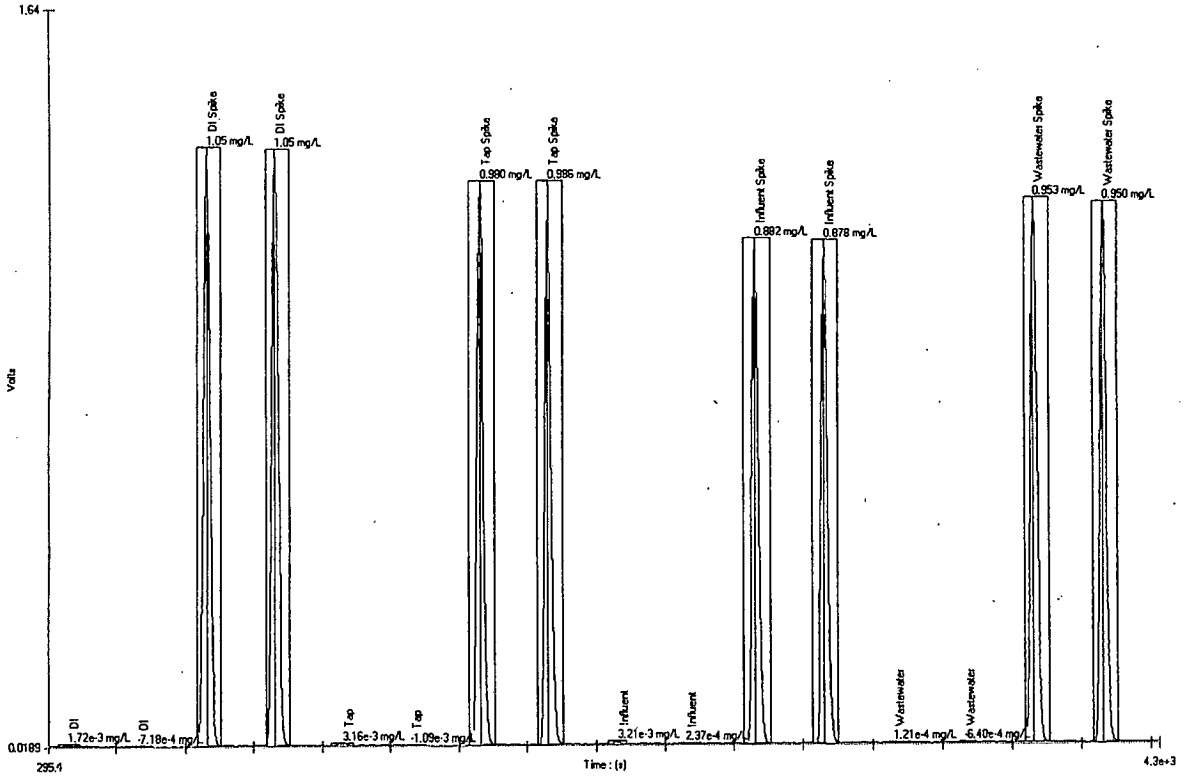


Carryover Study: 2.00 mg S/L standard followed by 3 blanks

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

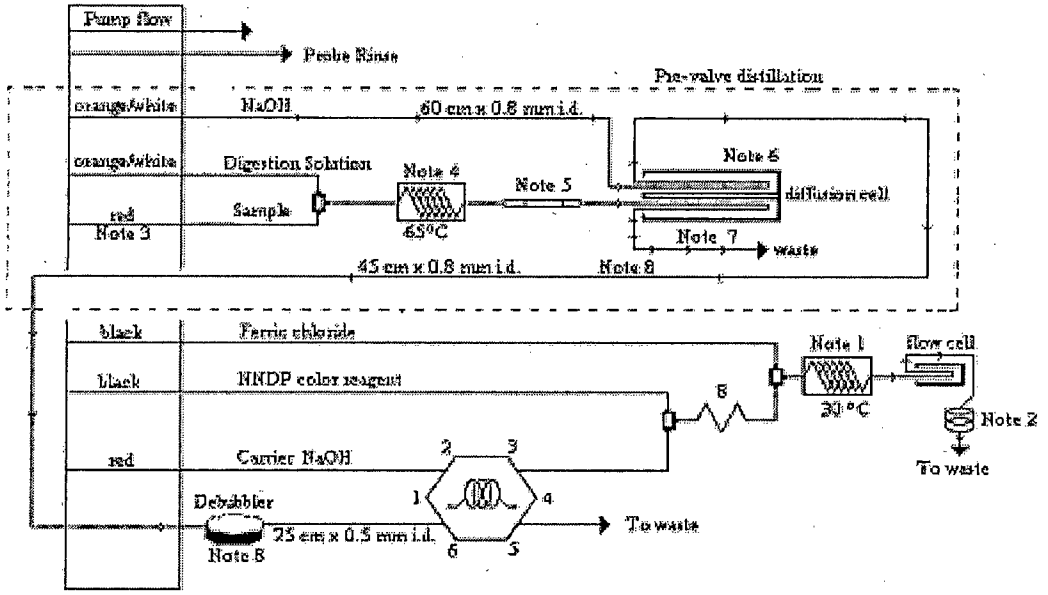
Acq. Date: 5 October 2007



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.

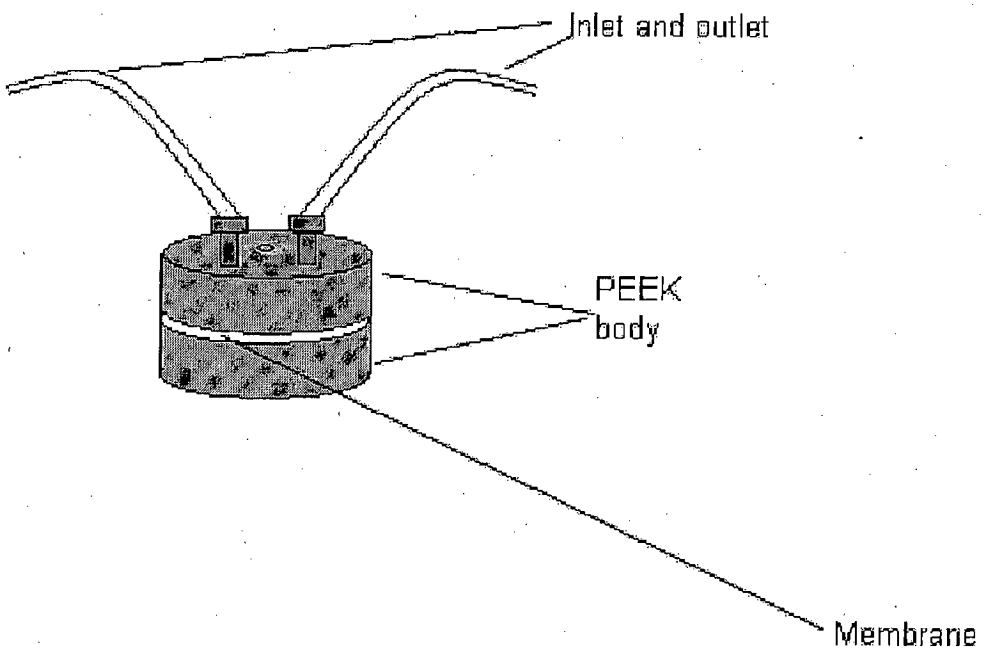
8: **168** cm of tubing on a 8 cm coil support

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)

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.

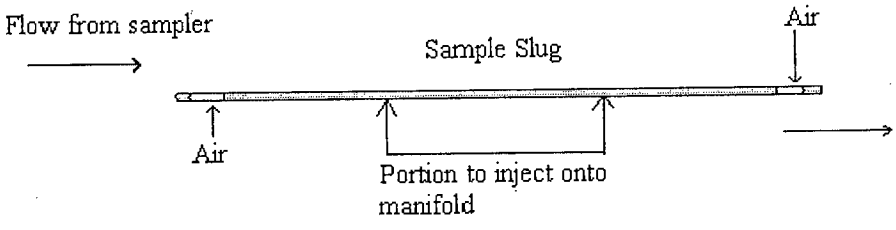
11.3 SYSTEM NOTES

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

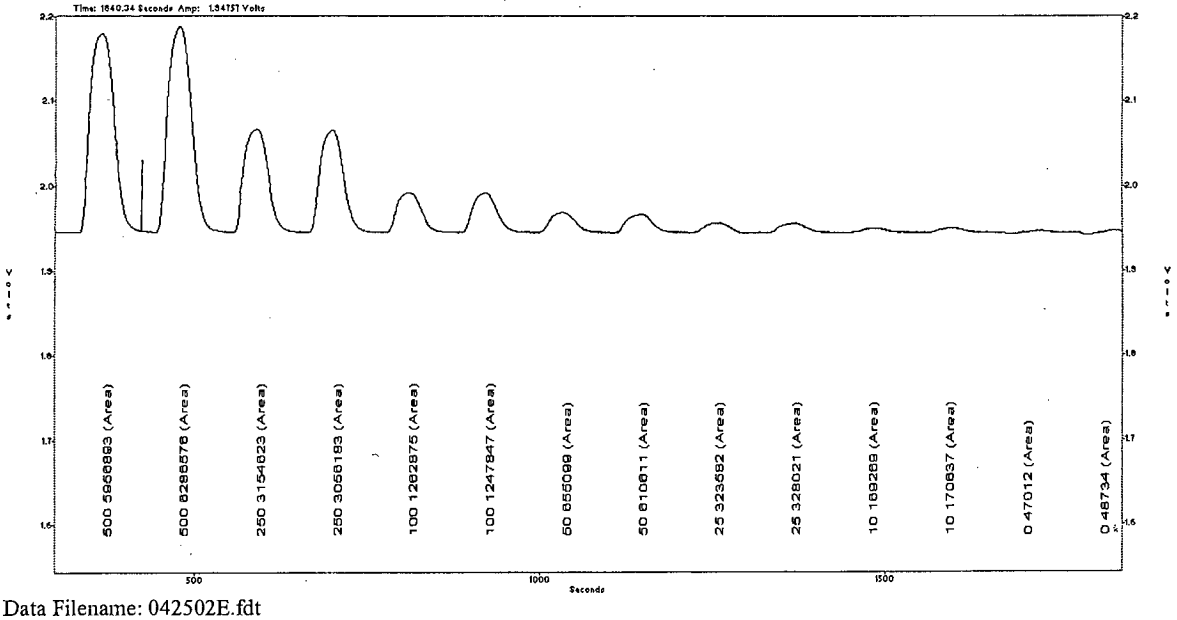
Valve Timing:

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

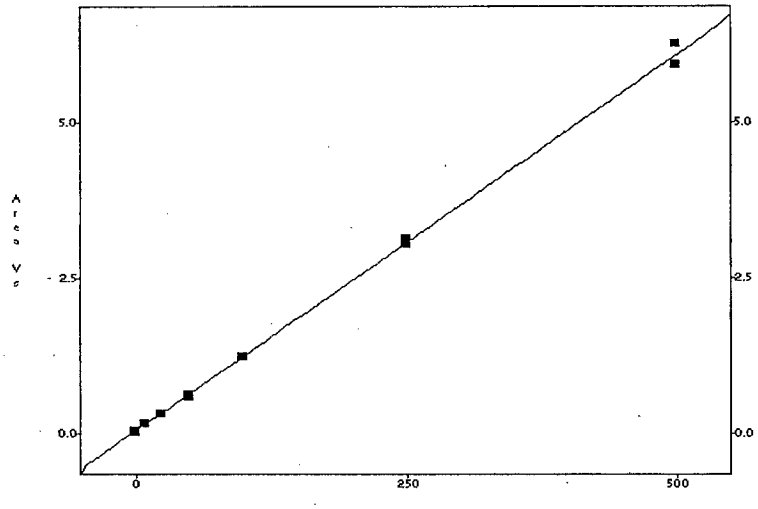
Calibration Data for Total Phosphorus

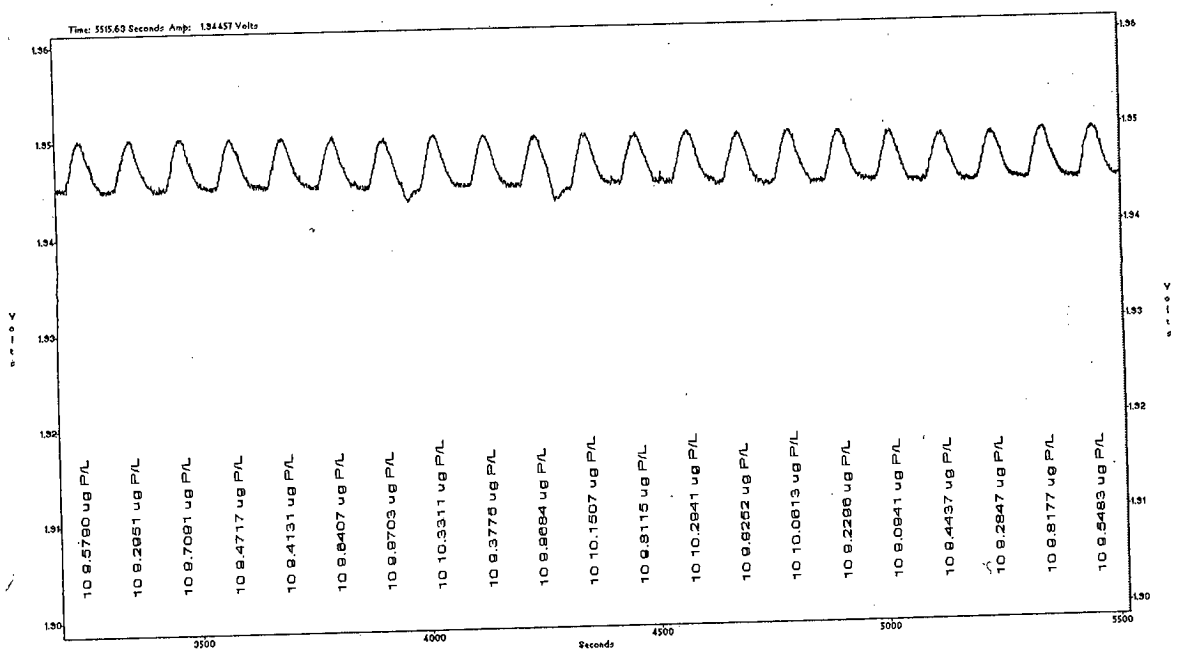


Data Filename: 042502E.fdt
Acq Date: 25 April 2002:

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	***





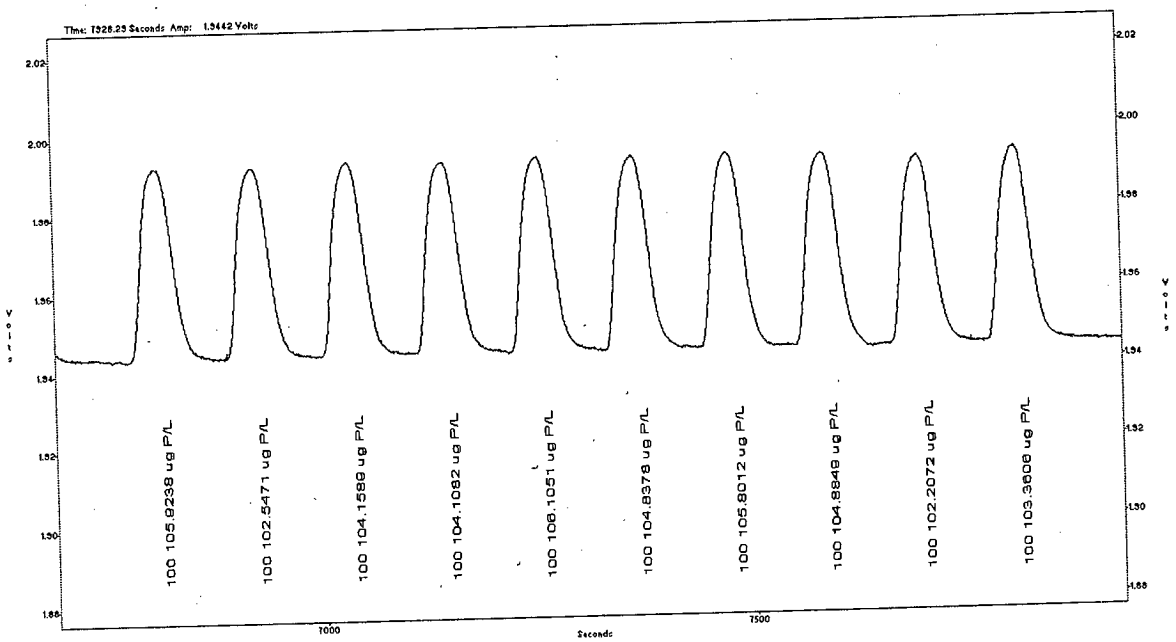
Method Detection Limit using 10 µg P/L as orthophosphate

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:



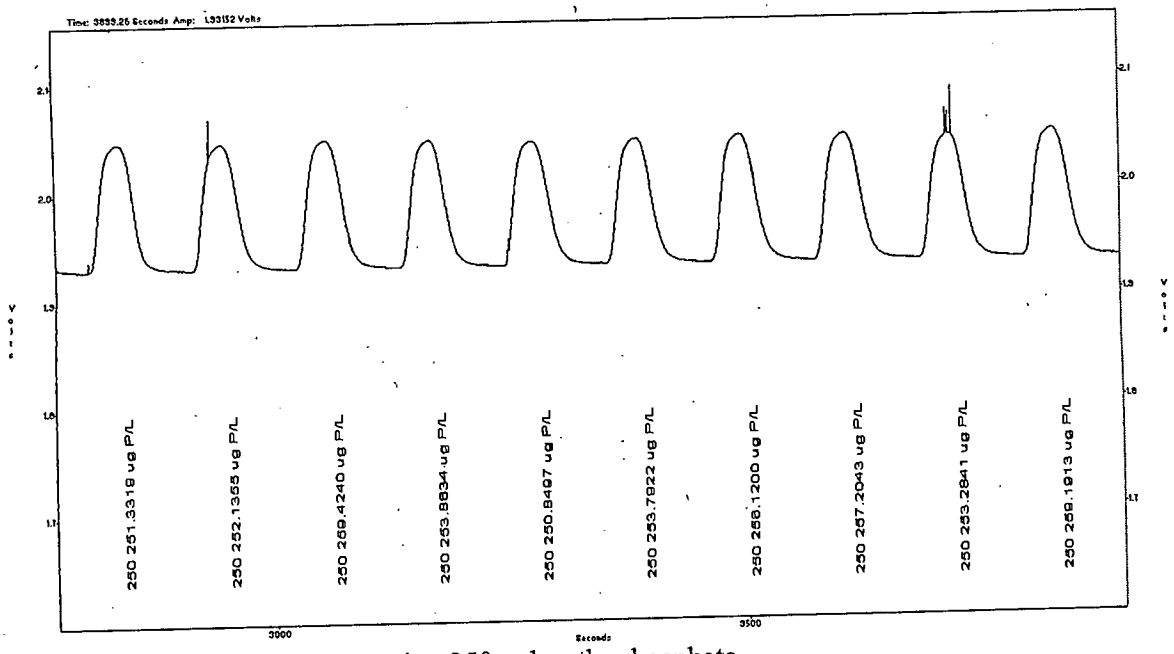
Precision data for phosphorus using 100 ppb orthophosphate

%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:



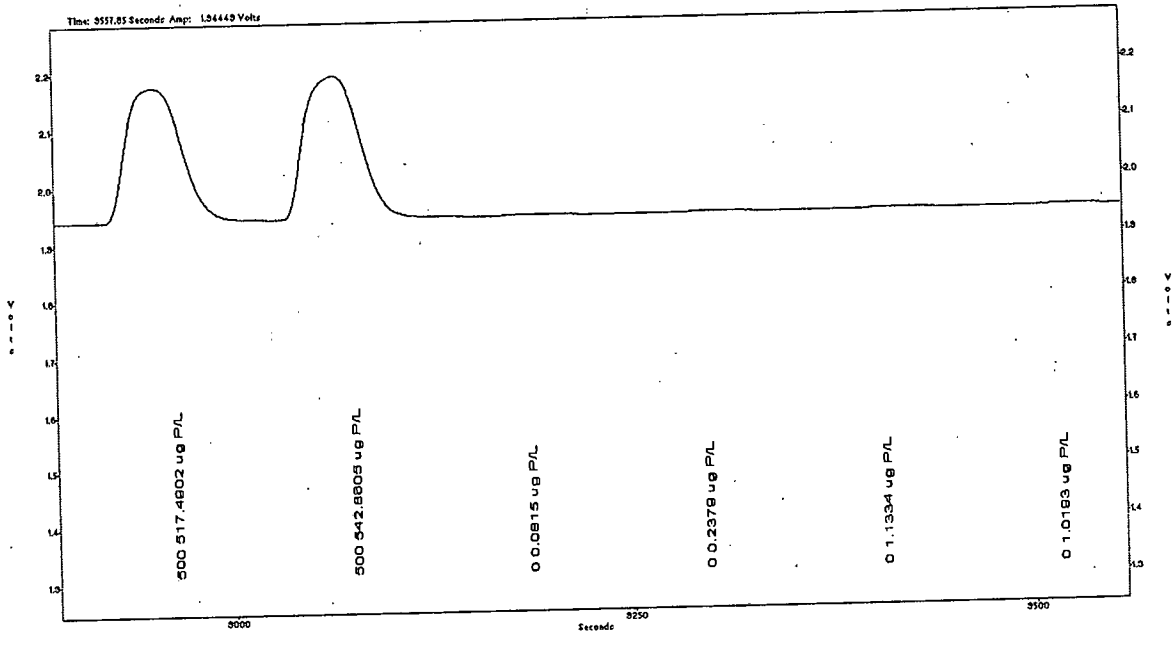
Precision data for phosphorus using 250 ppb orthophosphate

%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:



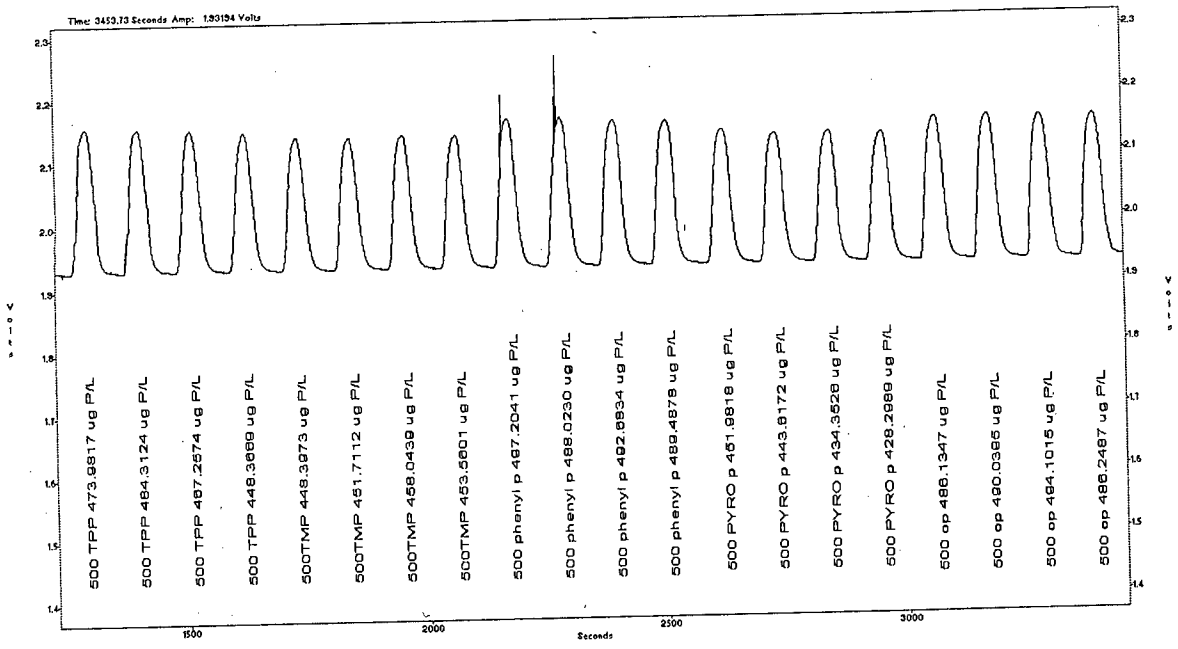
Carryover

Carryover passed

Data Filename: 042502E.fdt

Acq Date: 25 April 2002:

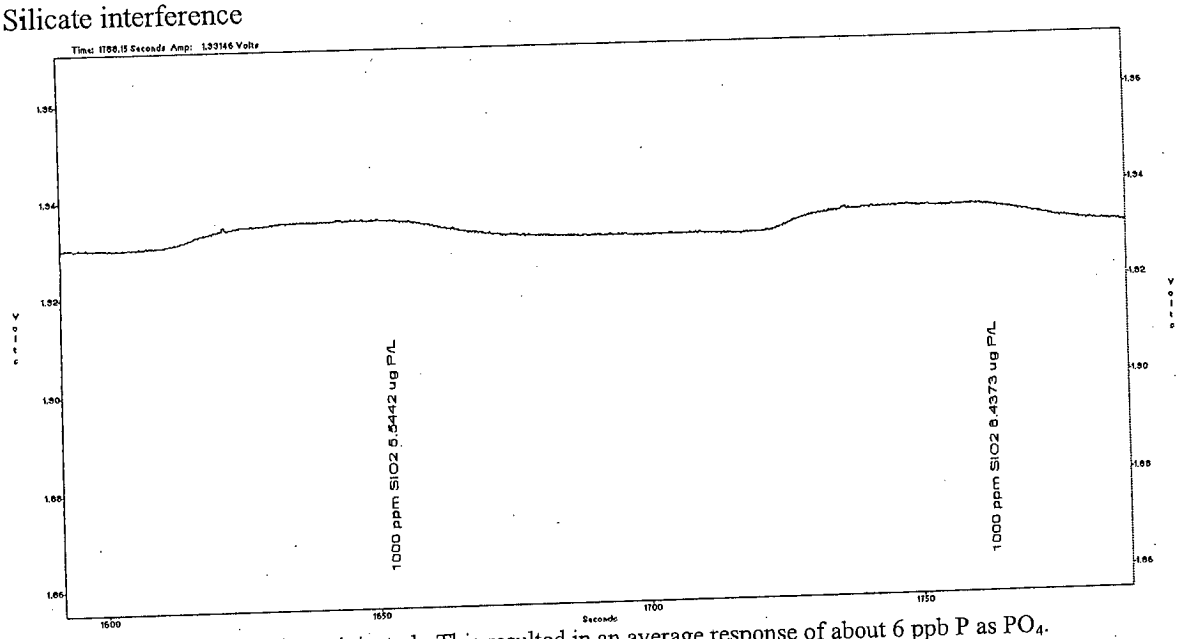
Recovery of Digestion Check Standards at 500 ppb



Data Filename: 050102C.fdt
Acq Date: 01 May 2002:

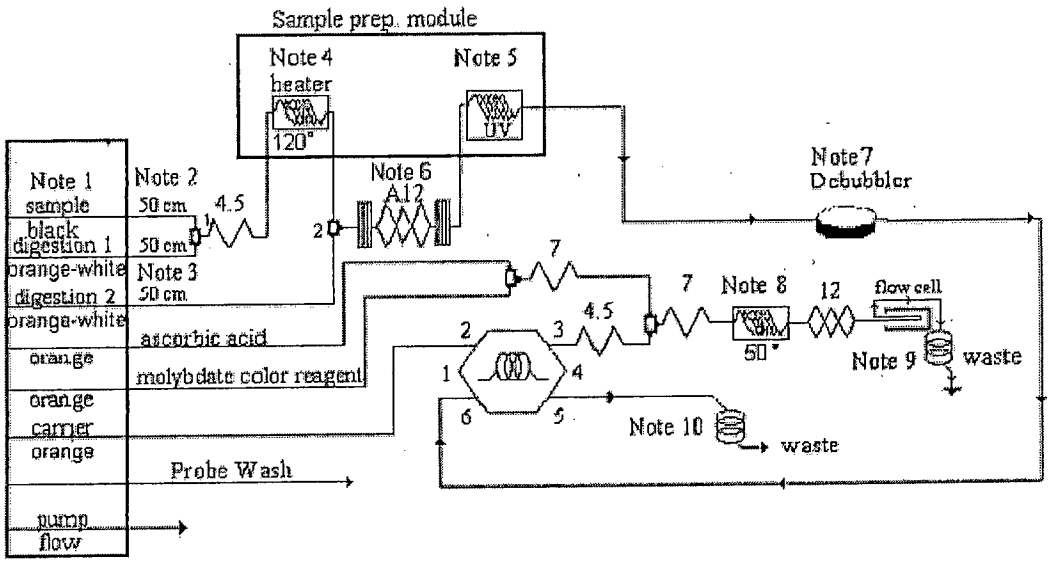
Sample	Known Value, µg P/L	Determined value, µg P/L	% recovery, relative to orthophosphorus
OrthoP	---	489.13	100%
TPP	500	468.48	95.77
Pyro P	500	439.56	89.87
Phenyl Phos	500	491.85	100.55
TMP	500	452.93	92.60

Silicate interference

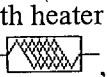


A 1000 ppm SiO_2 standard was injected. This resulted in an average response of about 6 ppb P as PO_4.
Conclusion: Silicate is not a significant interferent in this method. (Selectivity: 166,667)
Data Filename: 050102A.fdt
Acq Date: 01 May 2002

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

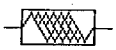
---

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.

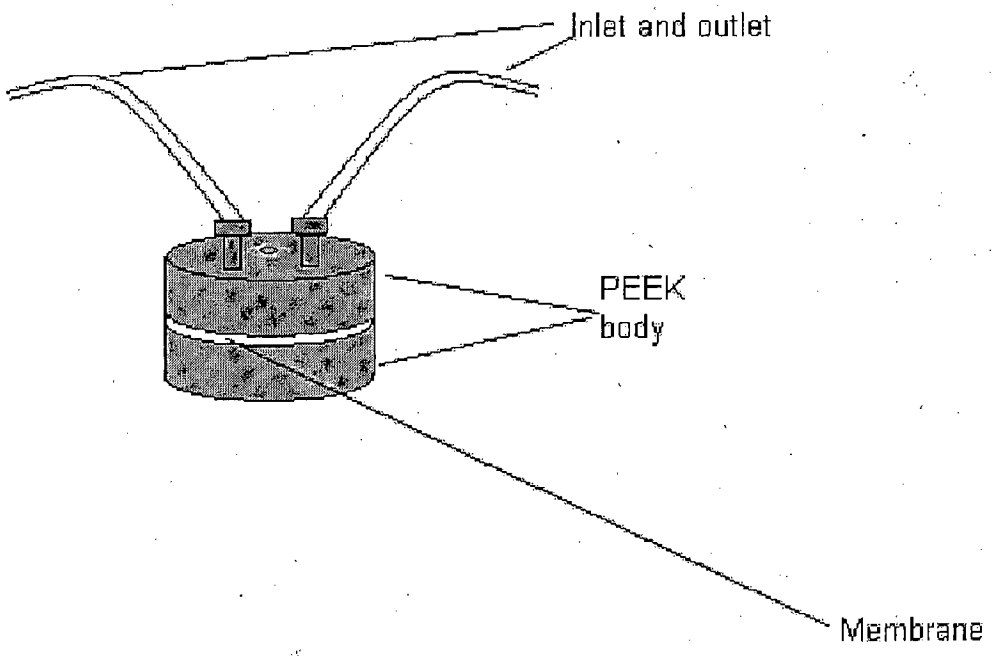
Note 7: **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing 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

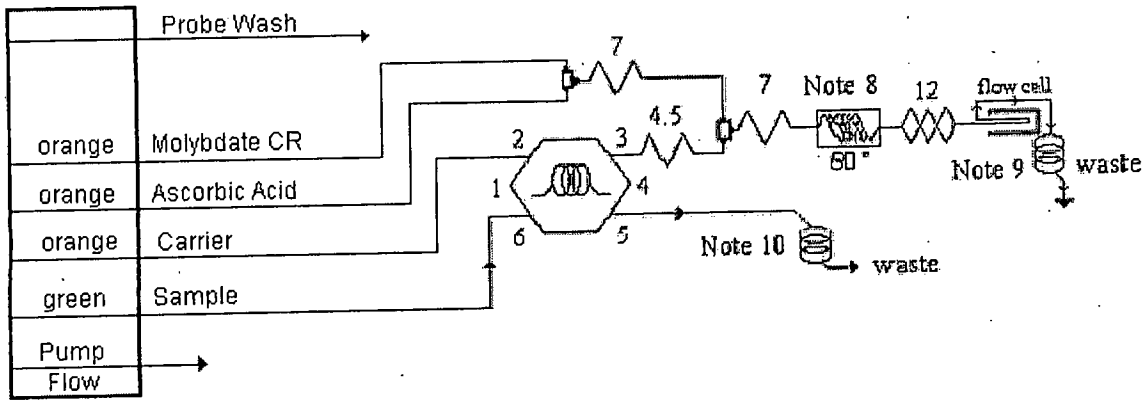
Sampler Timing:

Min. Probe in Wash Period:	5 s
Sample Period:	30 s

Valve Timing:

Load Period:	25 s
Inject Period:	55 s

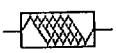
Ortho Phosphate manifold



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

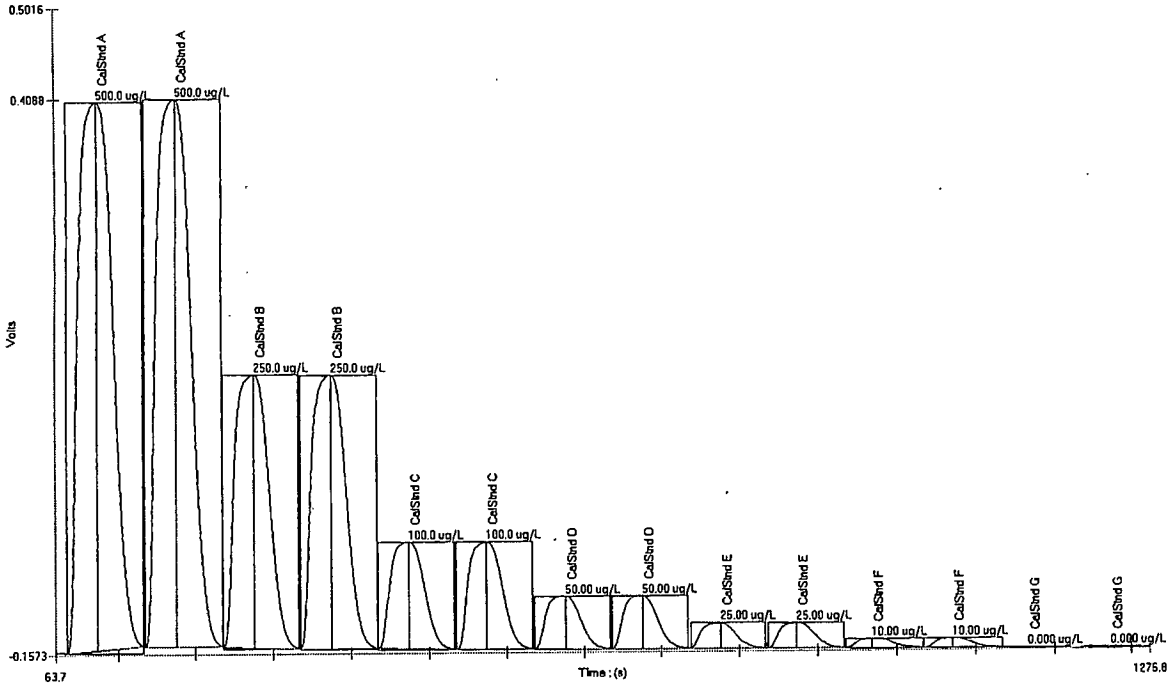
Apparatus: A sample prep module with heater and UV lamp, an injection valve, a 10 mm path length flow cell, a heater  , and a colorimetric detector module are required.

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

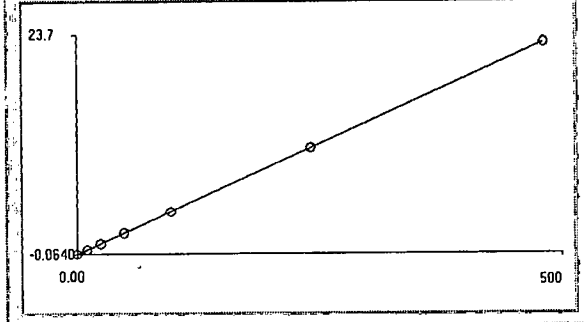


File Name: 12-3 cal support.omn
Acq. Date: 3 Dec 2010

Calibration Graph and Statistics

Calibration Results - Channel 4

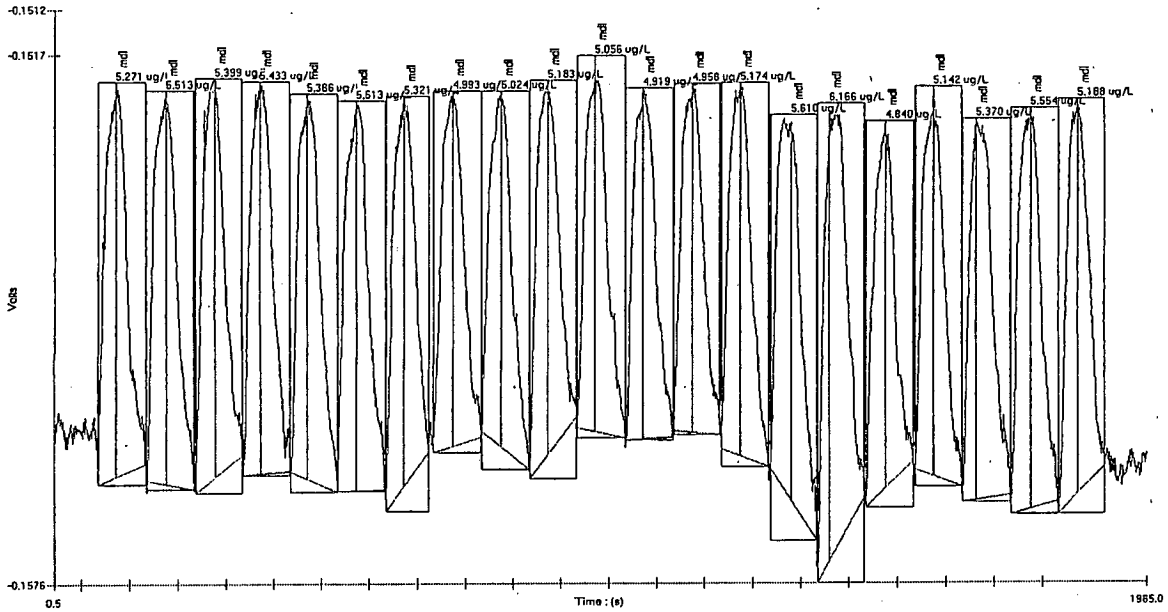
	Known Conc. (ug/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (ug/L)	Date	Time
1	500.0	1	23.70	0.5598	0.2	-0.2	☐	501.1	12/3/2010	7:19:49 AM
2	500.0	2	23.64	0.5585	0.2	9.1e-4	☐	500.0	12/3/2010	7:21:15 AM
3	250.0	1	11.77	0.2786	0.4	0.2	☐	249.5	12/3/2010	7:22:41 AM
4	250.0	2	11.84	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



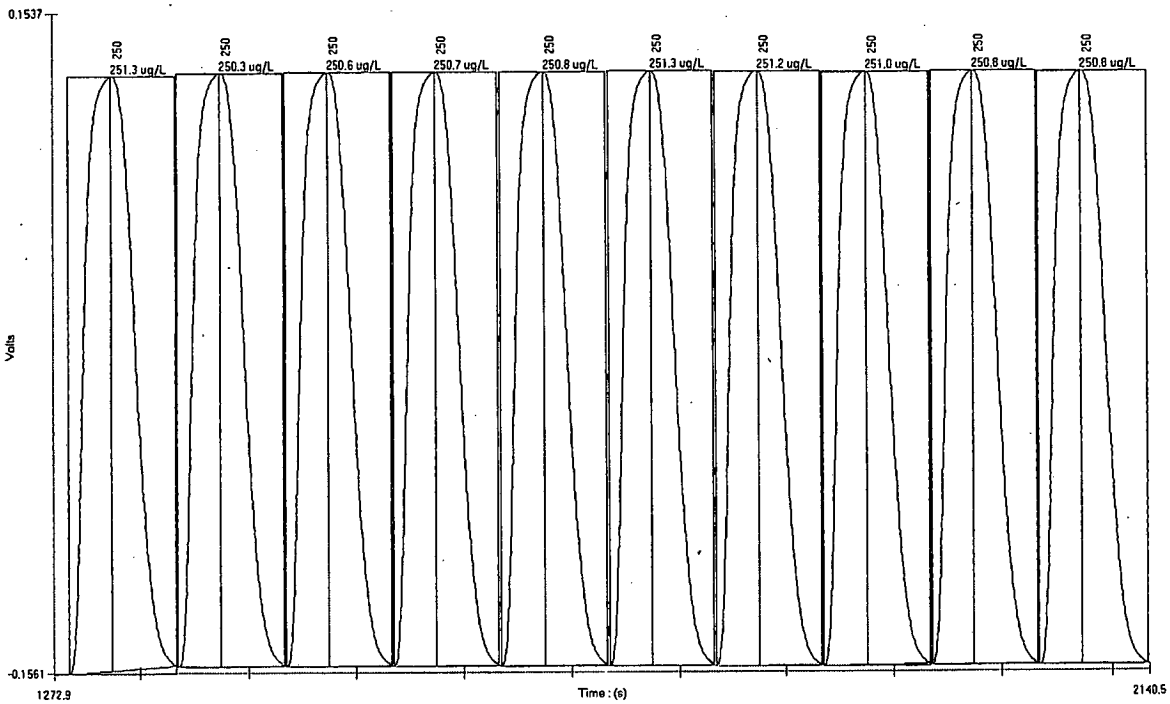
Method Detection Limit for Ortho Phosphate using a 5 µg P/L standard

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



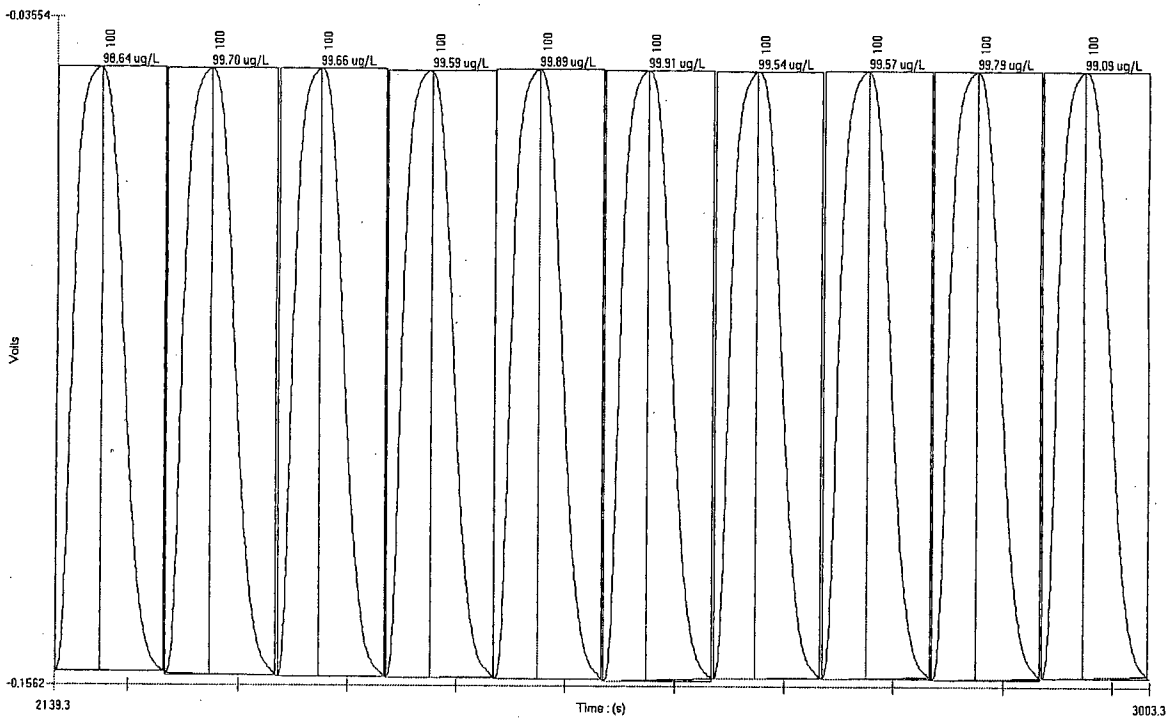
Precision Data for Ortho Phosphate using a 250 µg P/L standard

% 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



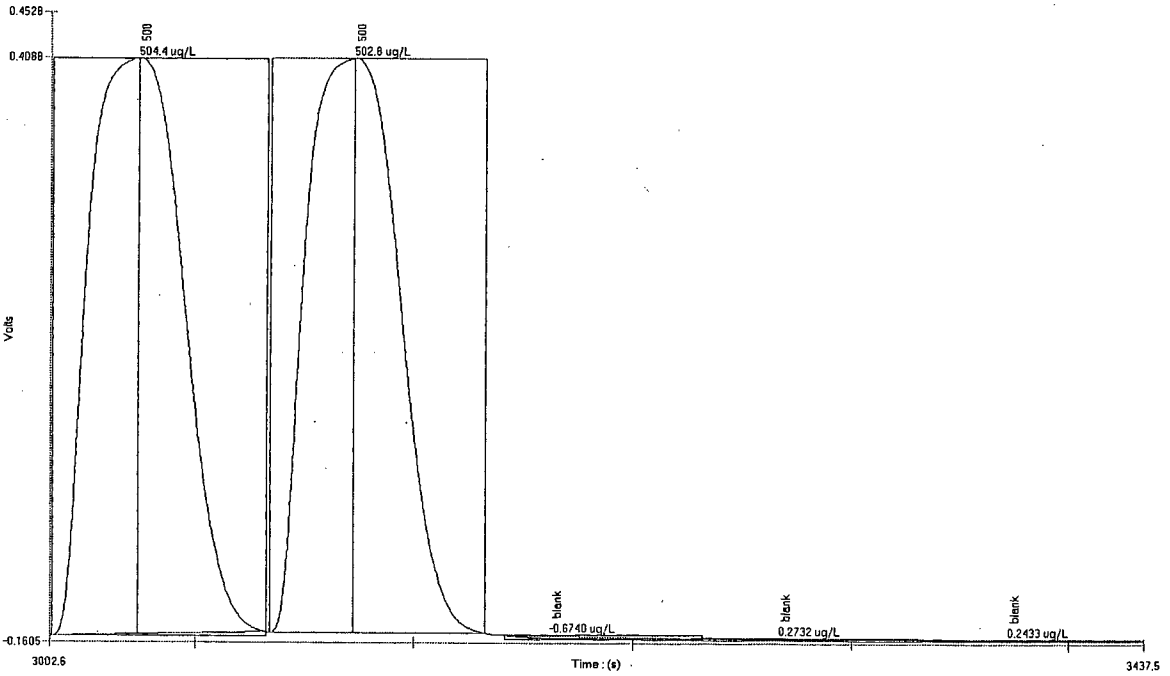
Precision Data for Ortho Phosphate using a 100 µg P/L standard

% 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 10-107-04-3-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~~ sodium ($K_2S_2O_8$). 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

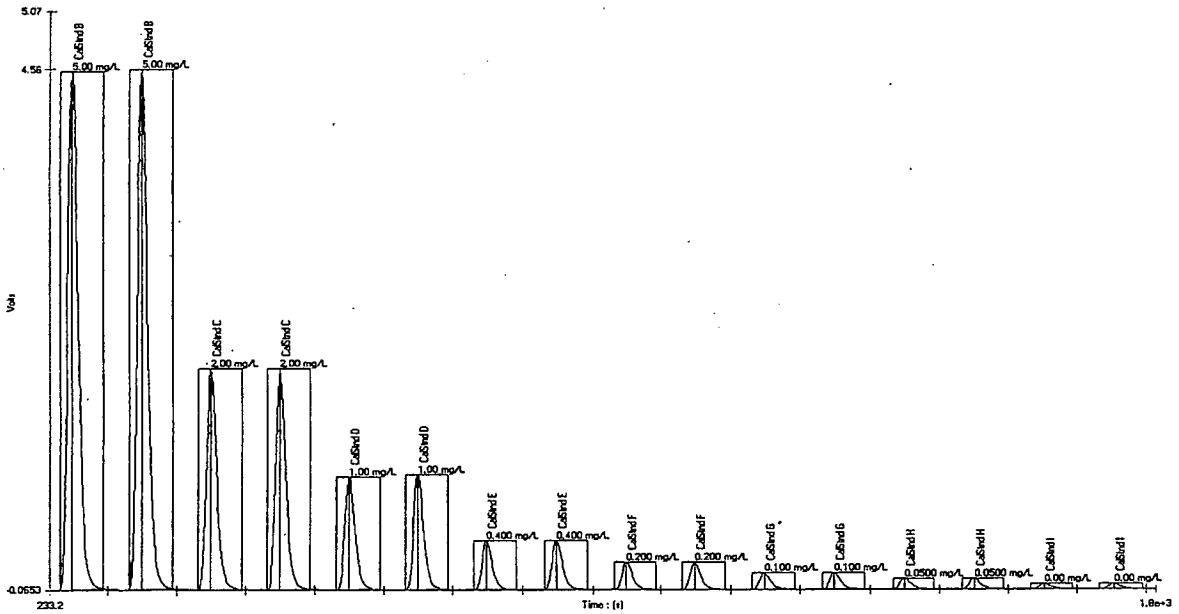
Valve Timing:

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



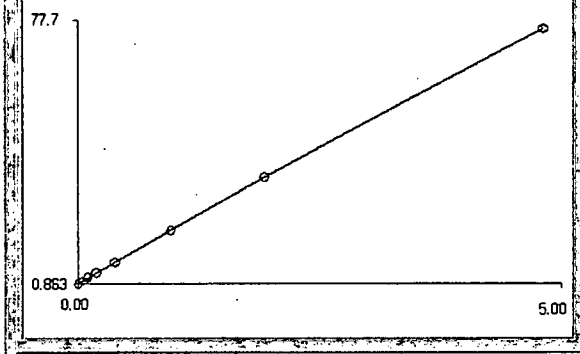
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

Calibration Graph and Statistics

Calibration Results - Channel 1

TN

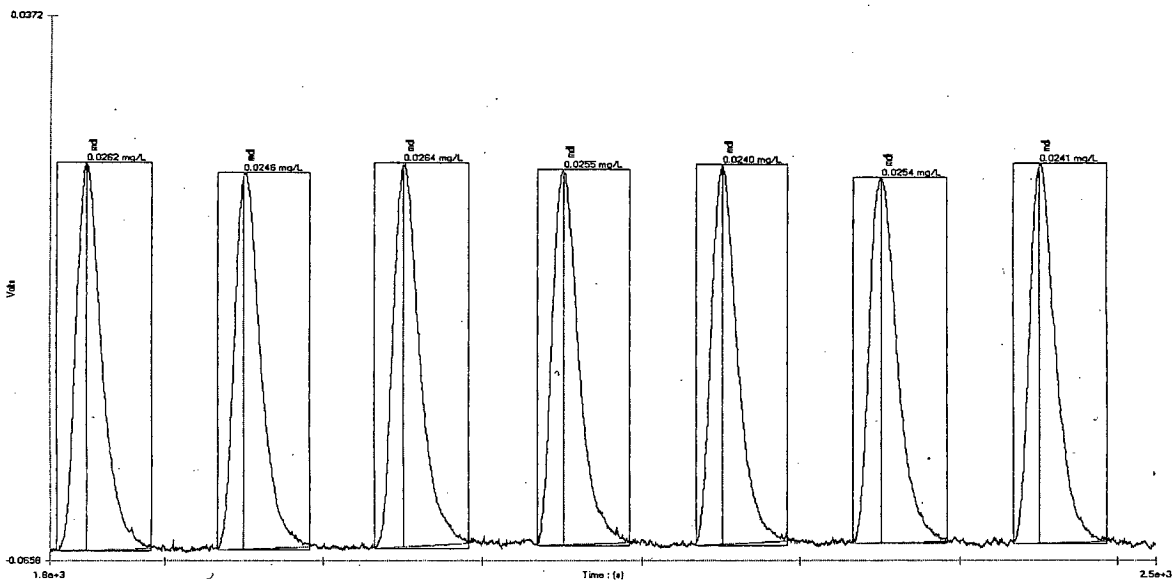
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	5.00	1	77.4	4.60	0.3	0.2	☐	4.99	11/19/2007	12:52:36 PM
2	5.00	2	77.7	4.62	0.3	-0.2	☐	5.01	11/19/2007	12:54:14 PM
3	2.00	1	32.9	1.98	0.3	-0.7	☐	2.01	11/19/2007	12:55:52 PM
4	2.00	2	32.8	1.97	0.3	-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...



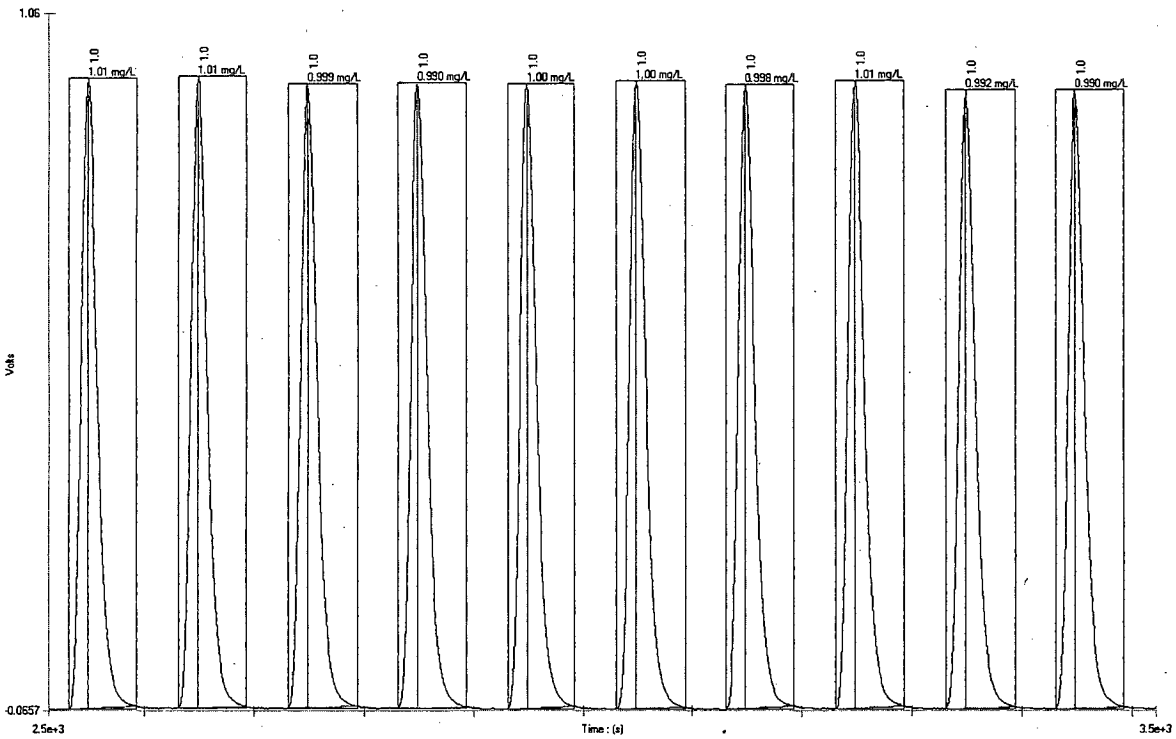
Method Detection Limit for Nitrogen using a 0.02 mg N/L standard

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



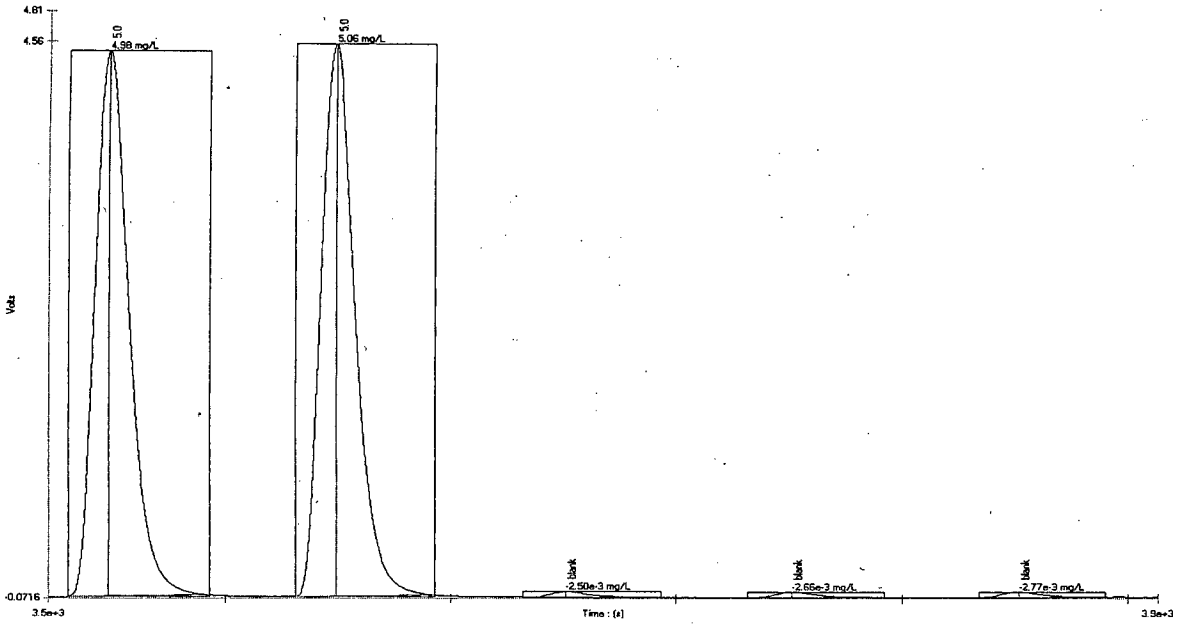
Precision Data for Nitrogen using a 1.0 mg N/L standard

% RSD =0.75

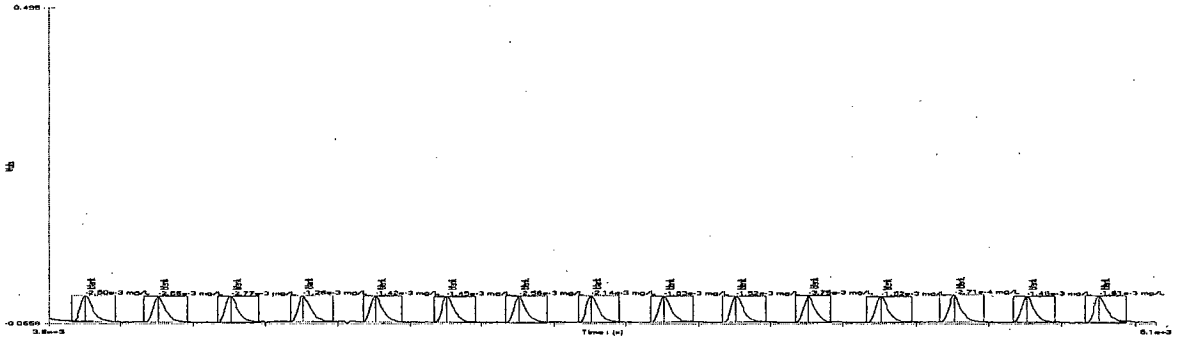
Standard Deviation (s) = 0.0075 mg N/L, Mean (x) = 1.00 mg N/L, Known Value = 1.00 mg N/L

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



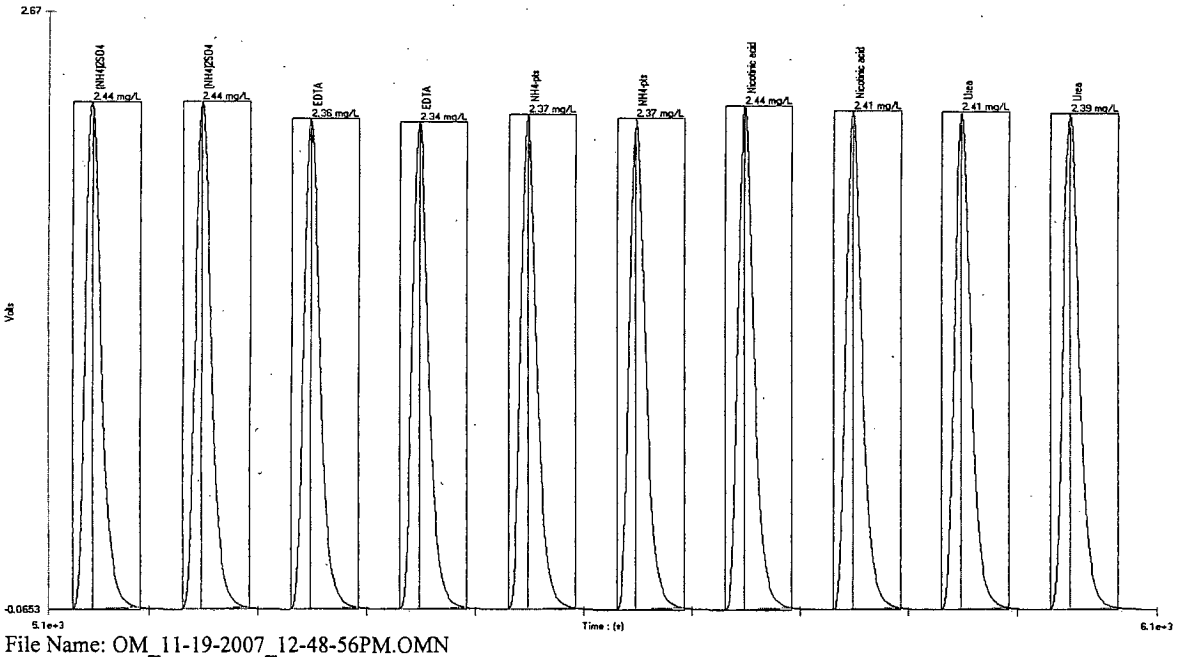
DIN Blanks

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

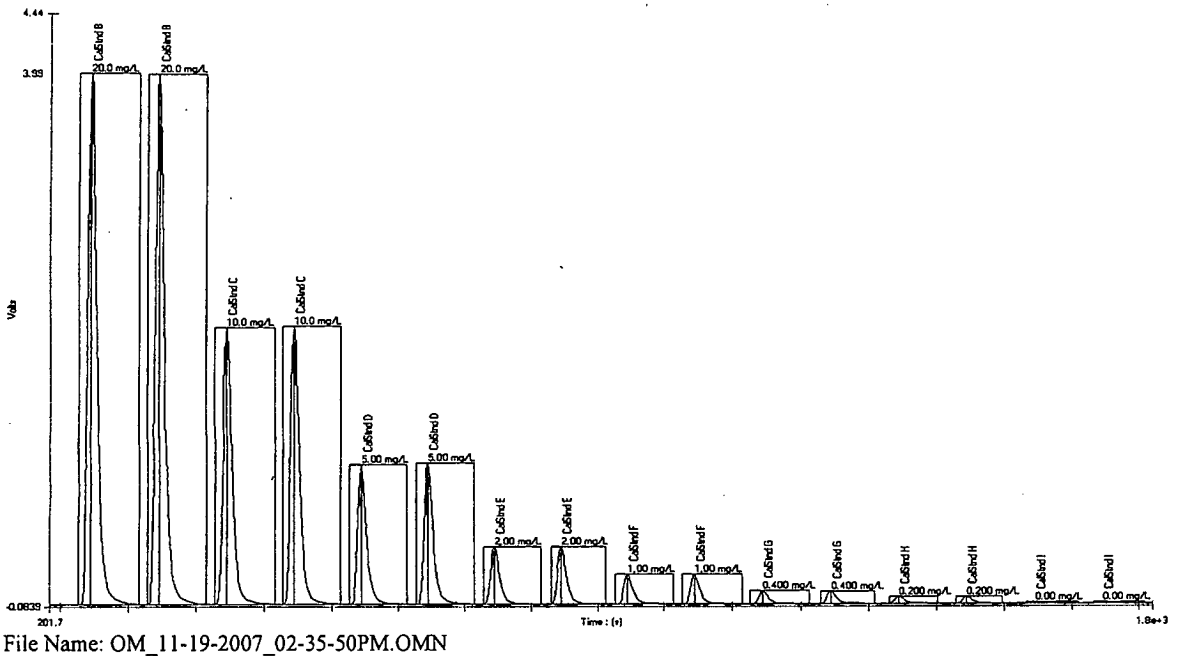
Nitrogen Form	Mean Result (mg N/L)	%Recovery
Ammonia	2.44	97.6
EDTA	2.35	94.0
NPTS*	2.37	94.8
Nicotinic Acid	2.43	97.0
Urea	2.40	96.0

* 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



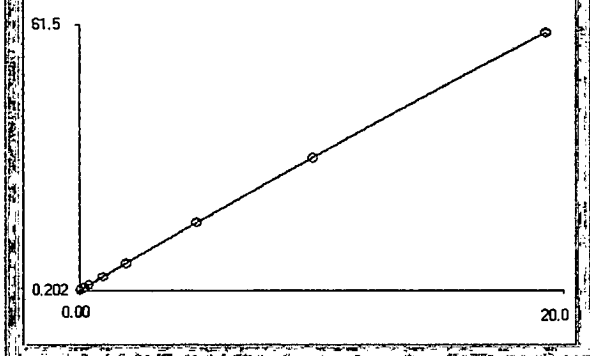
File Name: OM_11-19-2007_02-35-50PM.OMN
Acq. Date: 19 Nov 2007

Calibration Graph and Statistics

Calibration Results - Channel 1

TN

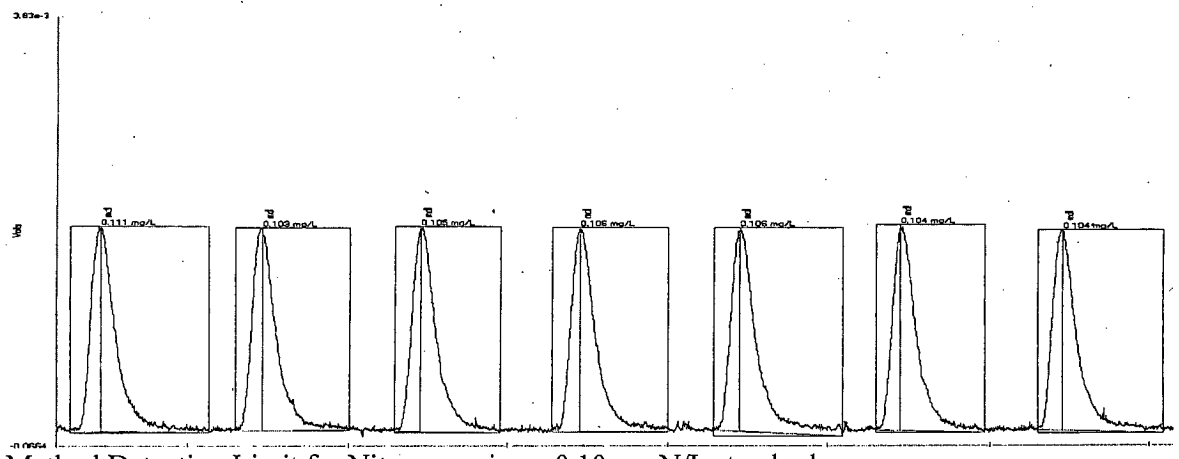
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	61.5	4.05	0.3	-0.2	☐	20.0	11/19/2007	2:39:32 PM
2	20.0	2	61.2	4.05	0.3	0.2	☐	20.0	11/19/2007	2:41:10 PM
3	10.0	1	31.7	2.11	0.1	0.3	☐	9.98	11/19/2007	2:42:47 PM
4	10.0	2	31.8	2.12	0.1	0.1	☐	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



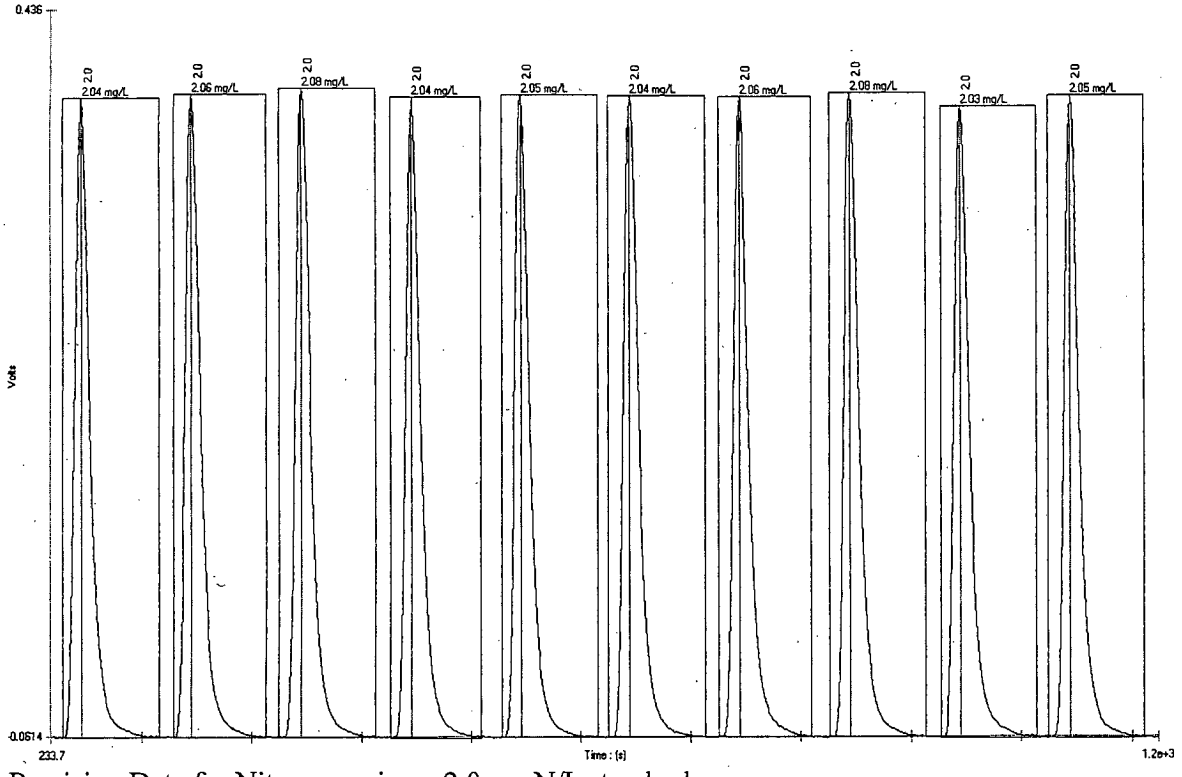
Method Detection Limit for Nitrogen using a 0.10 mg N/L standard

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



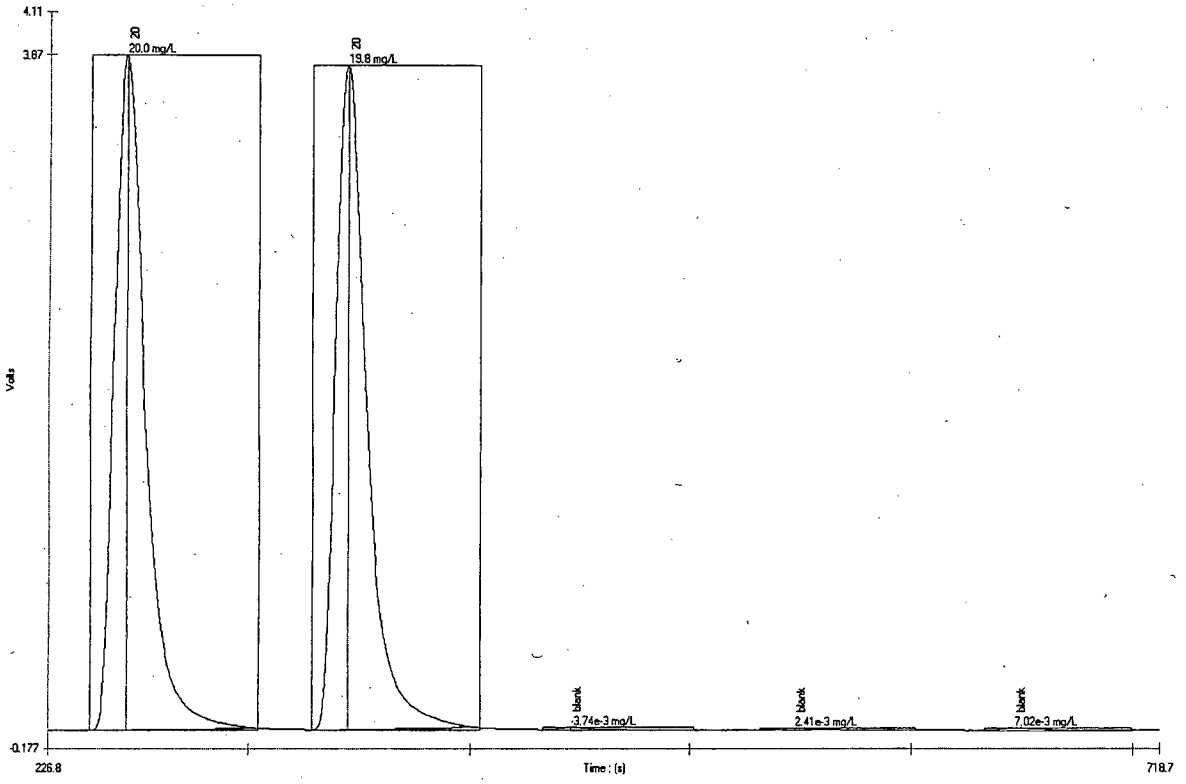
Precision Data for Nitrogen using a 2.0 mg N/L standard

% 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



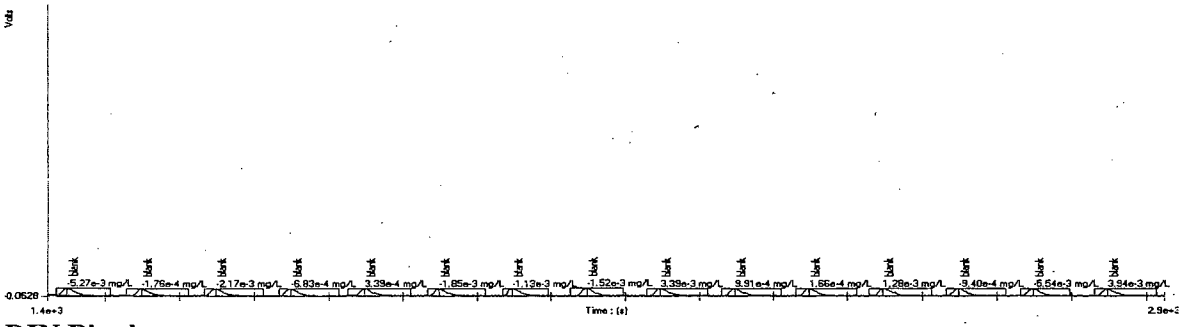
Carryover Study:

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.

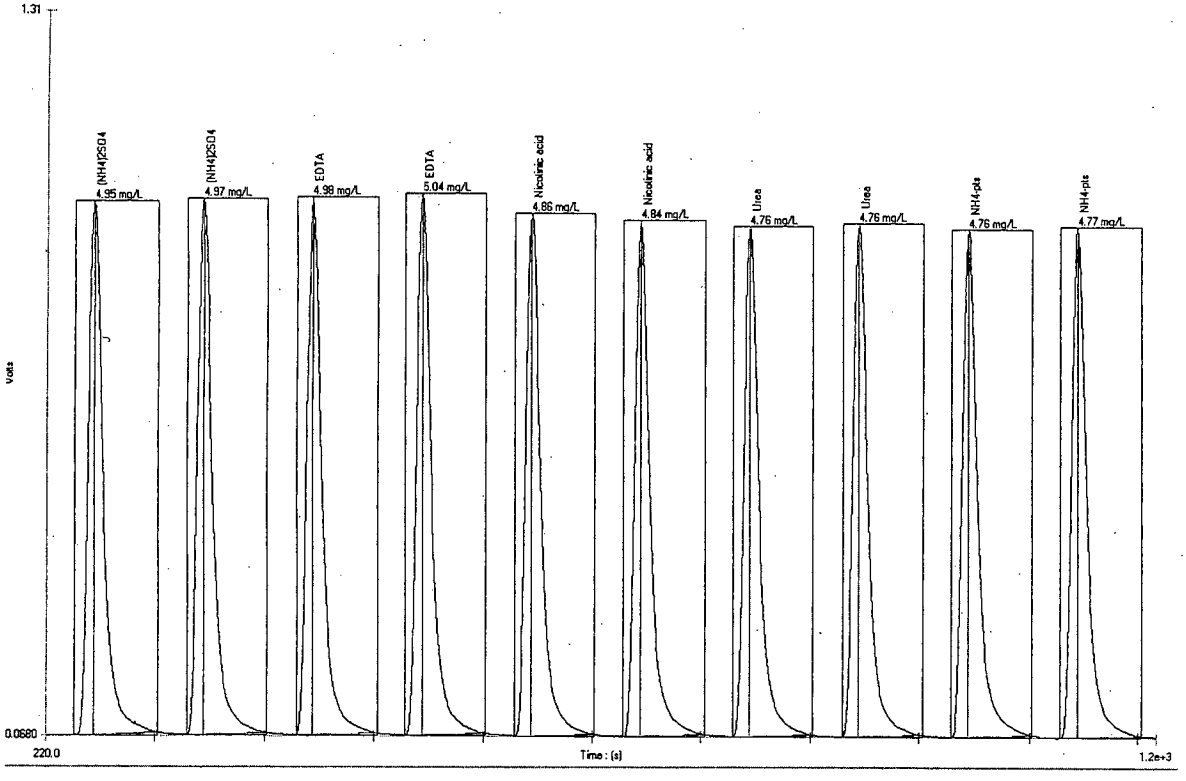
File Name: OM_11-20-2007_07-25-01AM.OMN

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

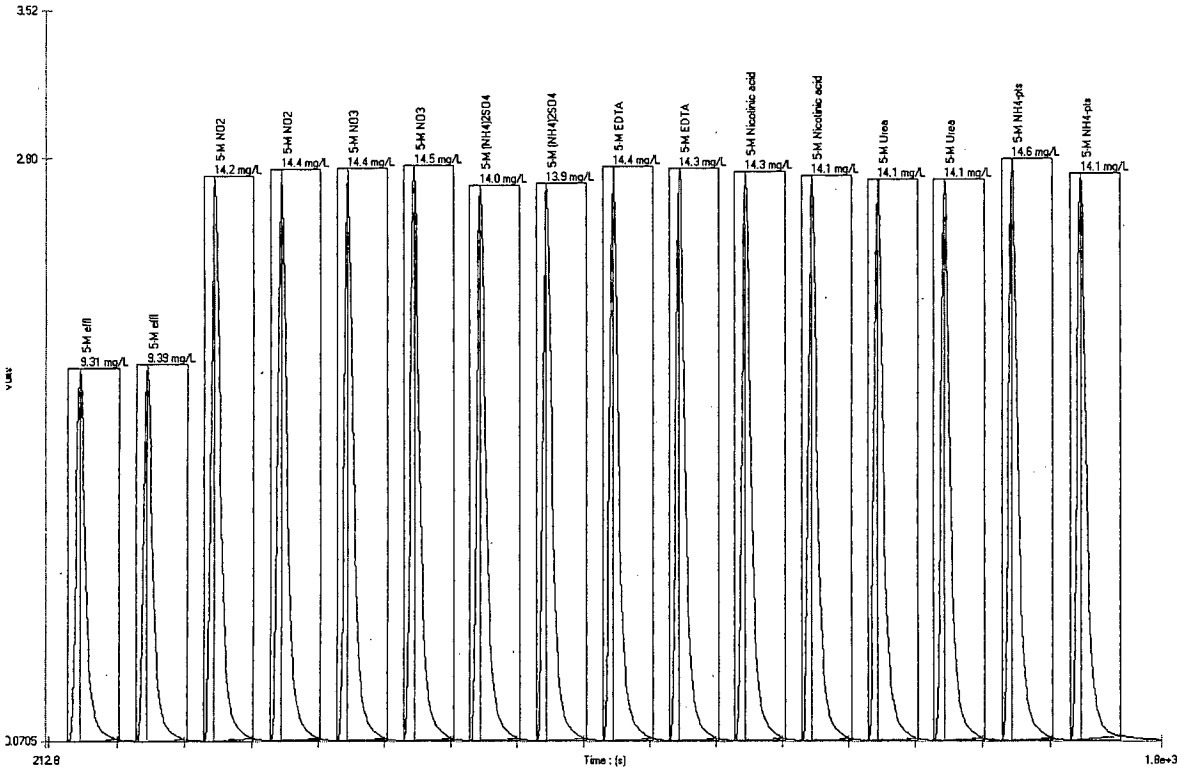
Initial total nitrogen concentration of wastewater was 9.35 mg N/L

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

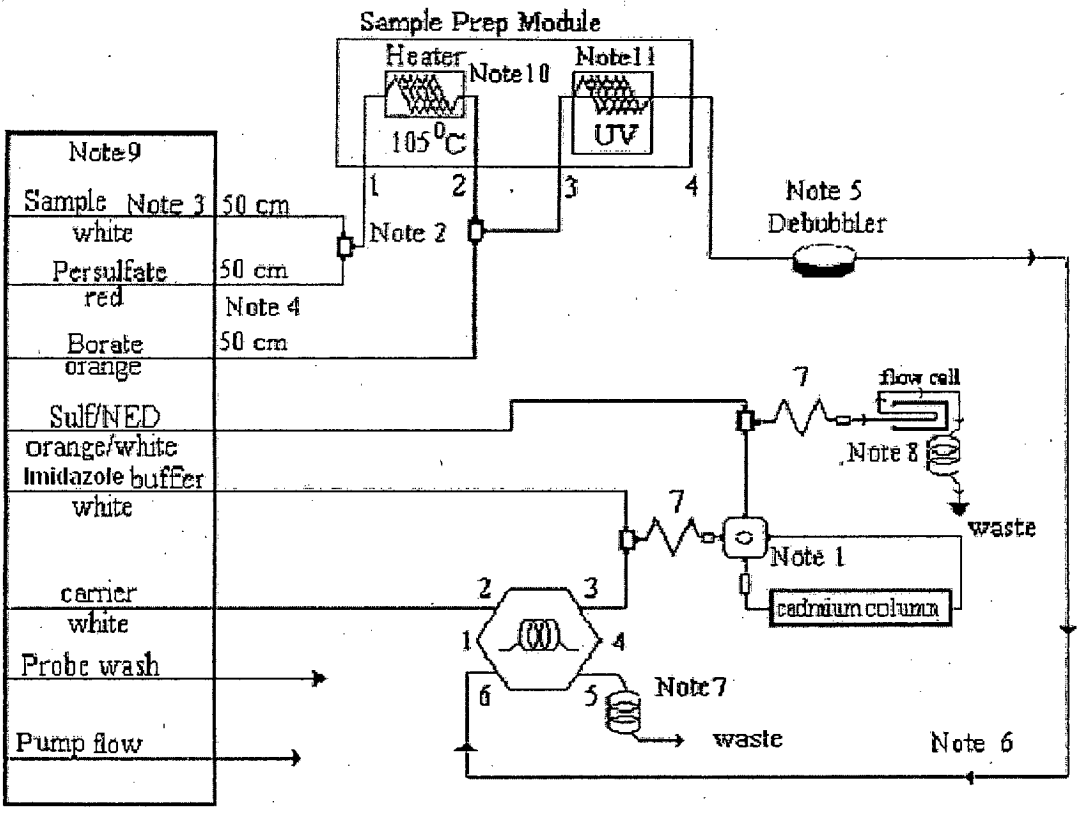
Conclusion: Spike recoveries of 92-102% were obtained using this method.



File Name: OM_11-26-2007_02-09-45PM.OMN

Acq. Date: 26 Nov 2007

17.3. TOTAL NITROGEN MANIFOLD DIAGRAM

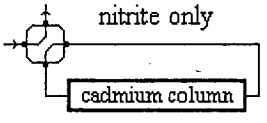


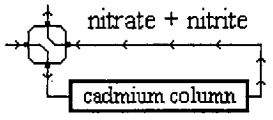
Carrier: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000/8500 Sample Loop: 50 cm Low Range
13 cm High Range (0.5 mm (0.022 in) i.d.)
Interference Filter: 540 nm

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.

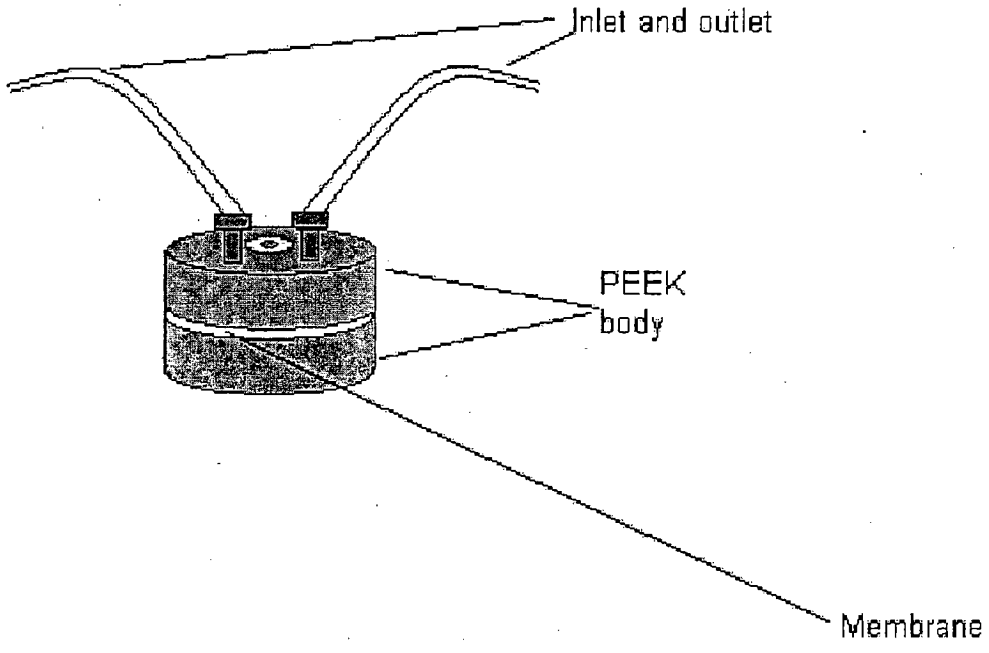
Note 8: The **200 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

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

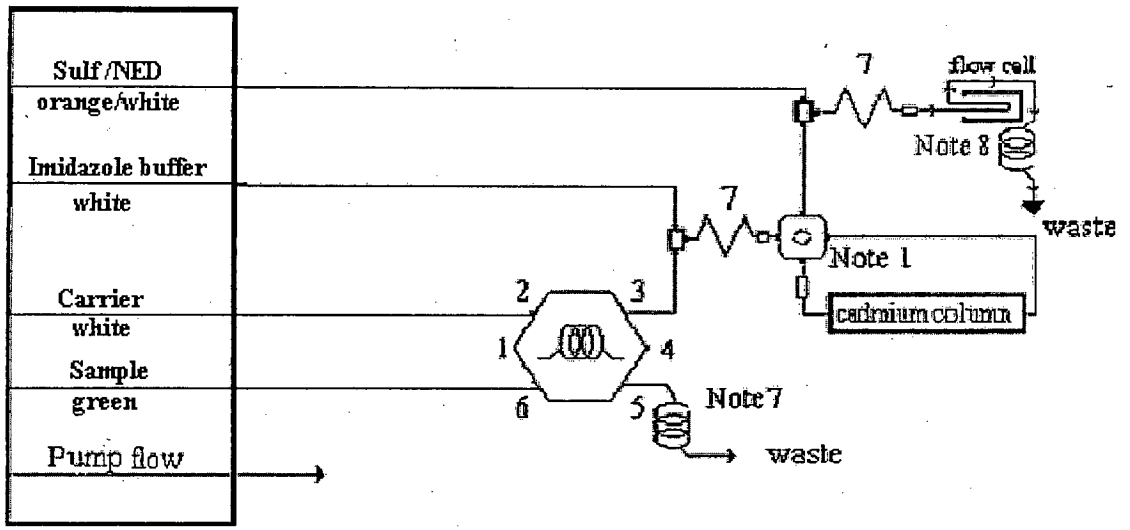
Sampler Timing:

Min. Probe in Wash Period: 15 s
Sample Period: 15 s

Valve Timing:

Load Period: 10 s
Inject Period: 70 s

Nitrate manifold

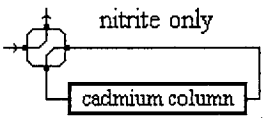


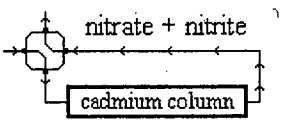
Carrier: **DI water**
Manifold Tubing: **0.8 mm (0.032 in) i.d.** This is **5.2 µL/cm.**
QC8000/8500 Sample Loop: 40 cm Low Range
Microloop High Range
Interference Filter: 540 nm

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

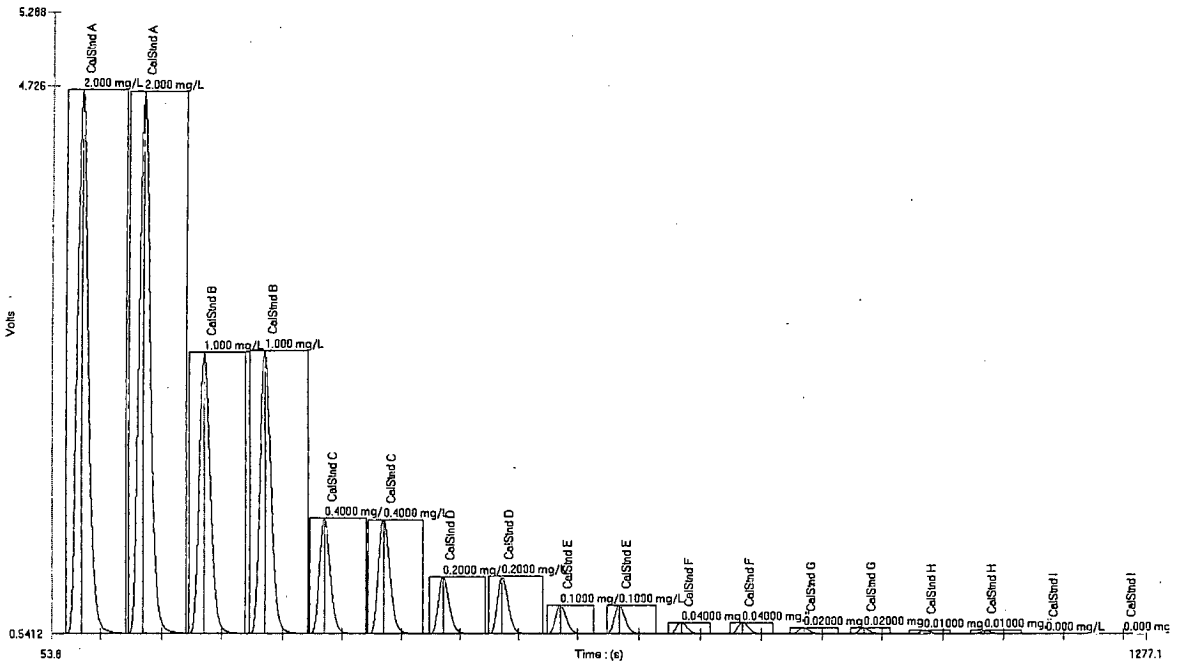
Note 1: This is a two state valve used to place the cadmium column in-line with the manifold.





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



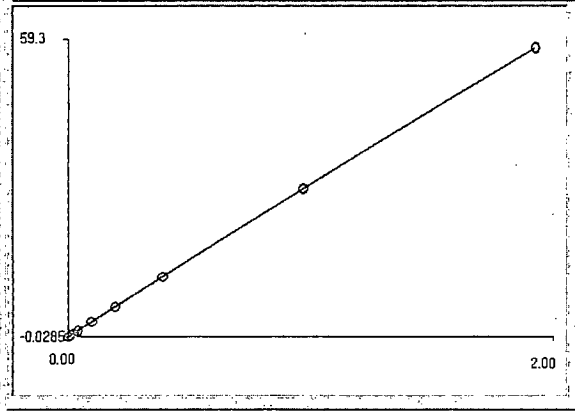
File Name: 12-2 cal support
Acq. Date: 2 Dec 2010

Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

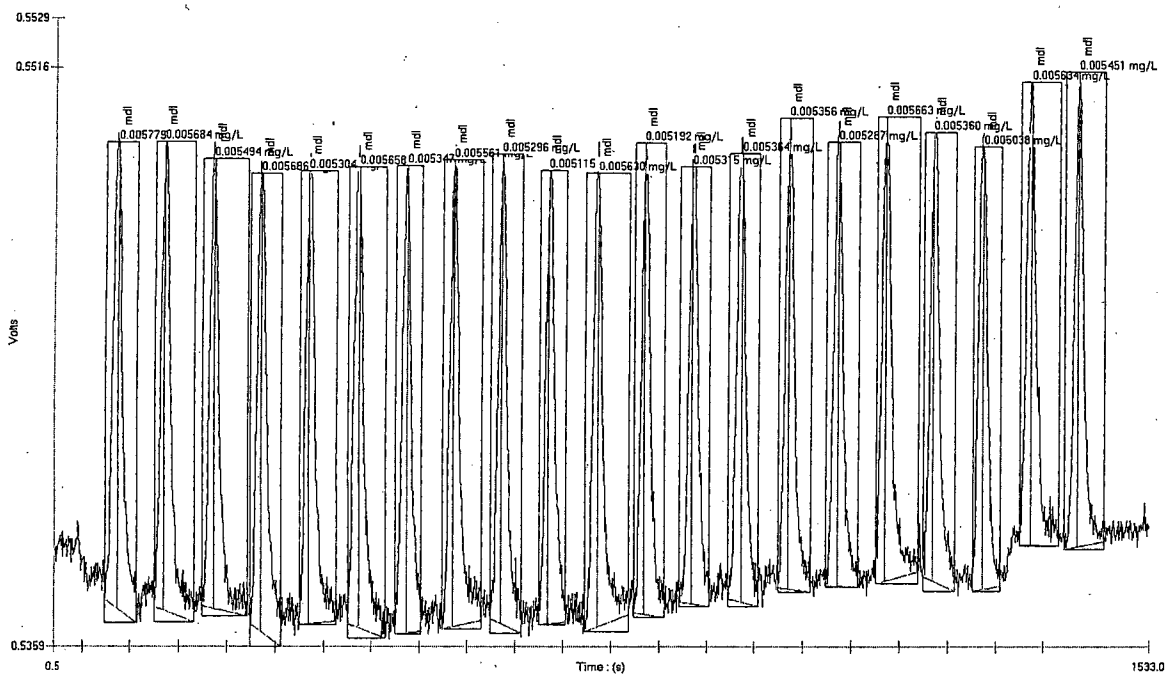
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	2.000	1	59.26	4.156	0.3	-0.2	☐	2.003	12/2/2010	12:01:09 PM
2	2.000	2	59.04	4.141	0.3	0.2	☐	1.995	12/2/2010	12:02:17 PM
3	1.000	1	30.31	2.151	0.4	0.1	☐	0.9992	12/2/2010	12:03:24 PM
4	1.000	2	30.47	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



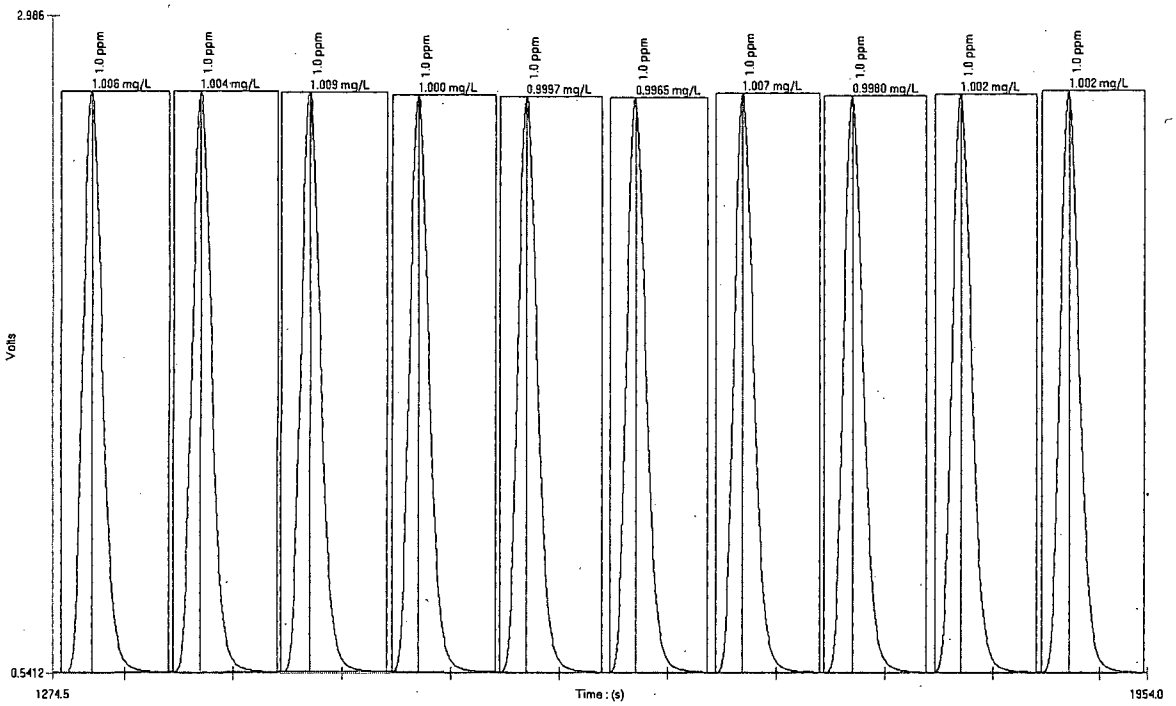
Method Detection Limit for Nitrate/Nitrite using a 0.005 mg N/L standard

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



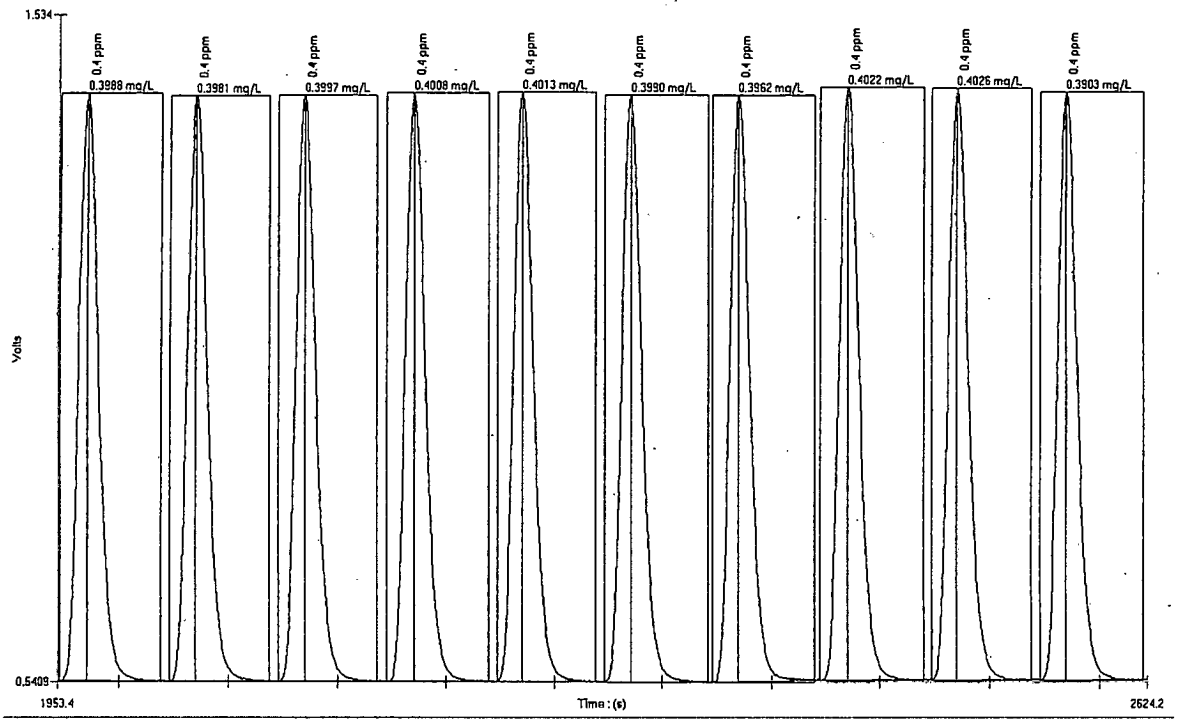
Precision Data for Nitrate/Nitrite using a 1.0 mg N/L standard

% 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



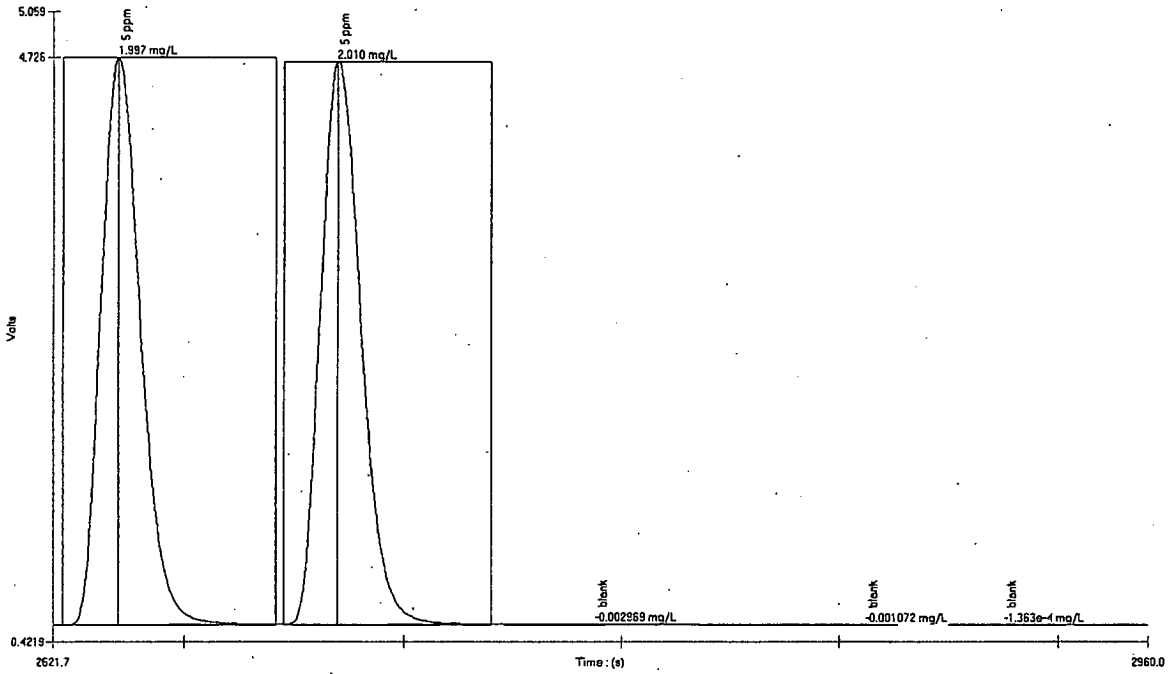
Precision Data for Nitrate/Nitrite using a 0.4 mg N/L standard

% 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:

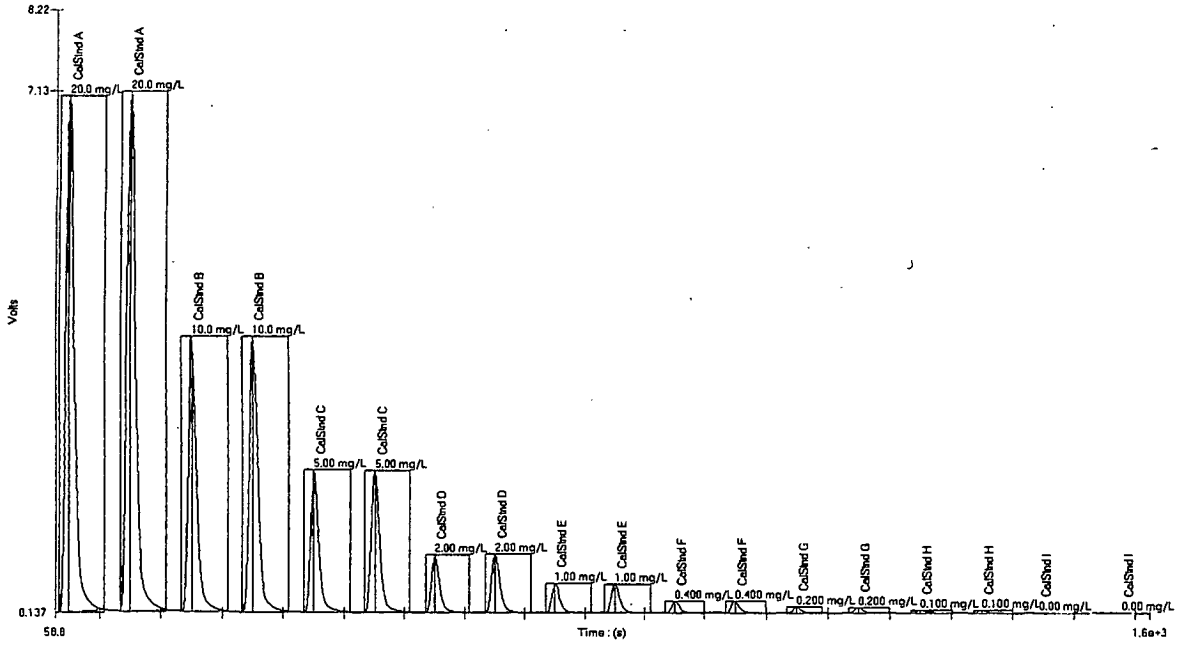
Two 2.0 mg N/L standards followed by three blanks

Carryover Passed

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010

Calibration Data for Nitrate/Nitrite High Range



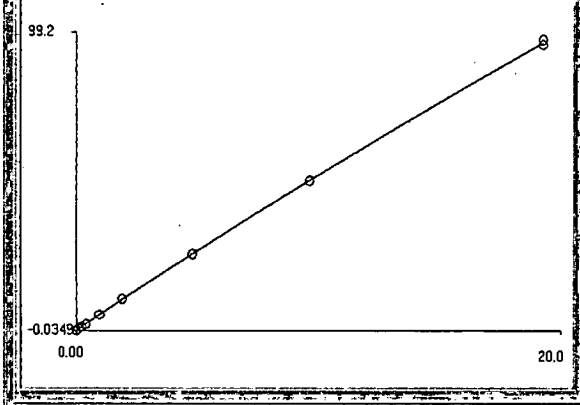
File Name: 11-12 cal HR.omn
Acq. Date: 12 Nov 2009

Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

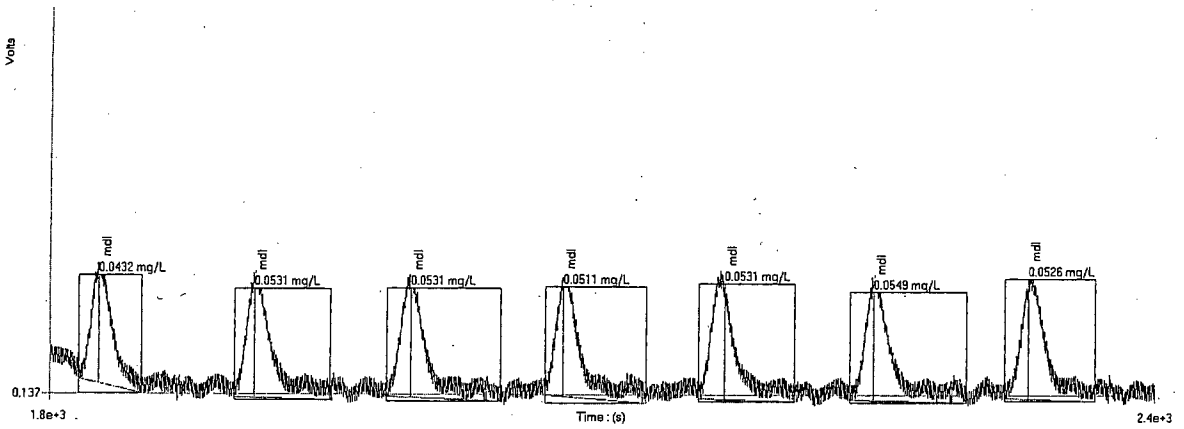
	Known Conc. (mg/L)	Rep.	Peak Area (V.s)	Peak Height (V)	% RSD	% Resid.	Unused	Det. Conc (mg/L)	Date	Time
1	20.0	1	97.5	6.92	1.2	0.7	☐	19.8	11/12/2009	7:55:43 AM
2	20.0	2	99.2	6.97	1.2	-1.0	☐	20.2	11/12/2009	7:57:10 AM
3	10.0	1	51.0	3.70	0.4	0.7	☐	9.95	11/12/2009	7:58:39 AM
4	10.0	2	51.3	3.70	0.4	0.1	☐	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



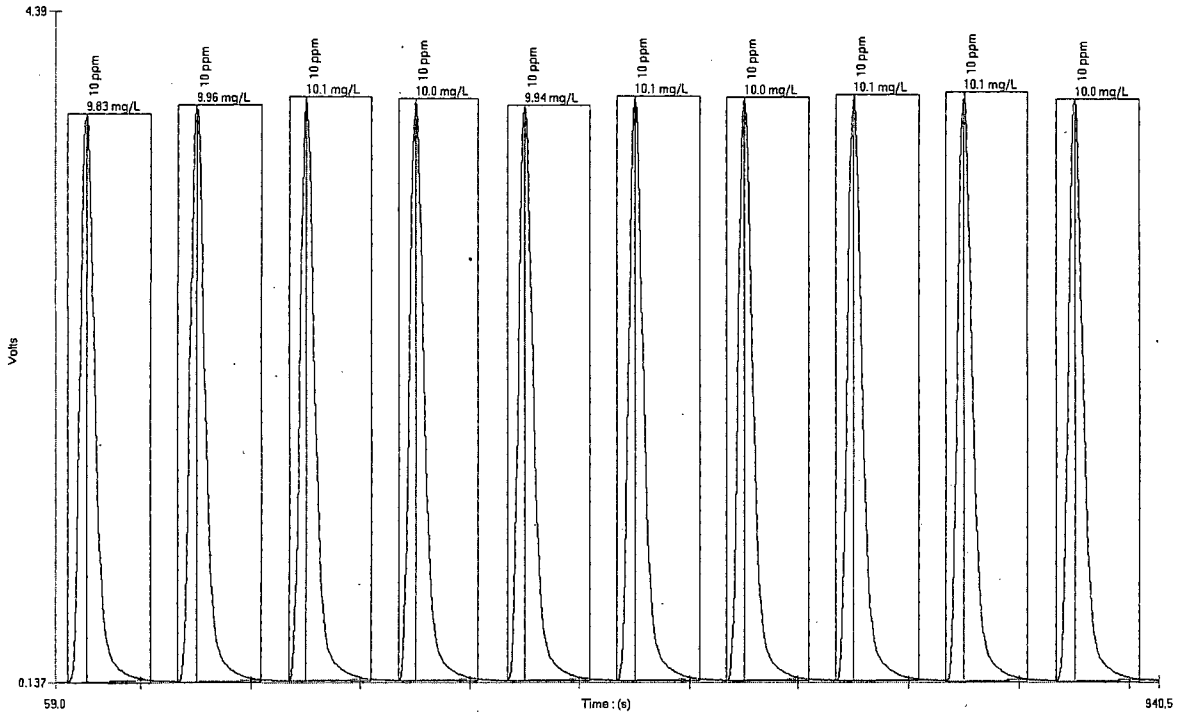
Method Detection Limit for Nitrate/Nitrite using a 0.05 mg N/L standard

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



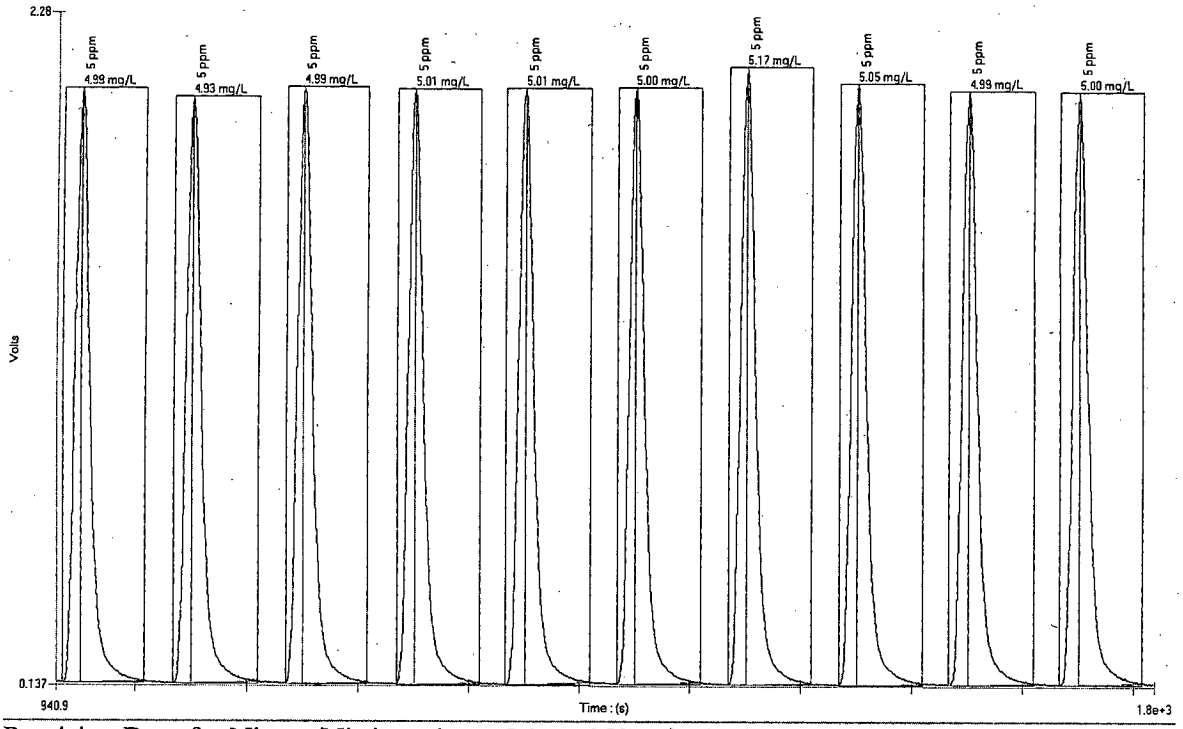
Precision Data for Nitrate/Nitrite using a 10.0 mg N/L standard

% 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



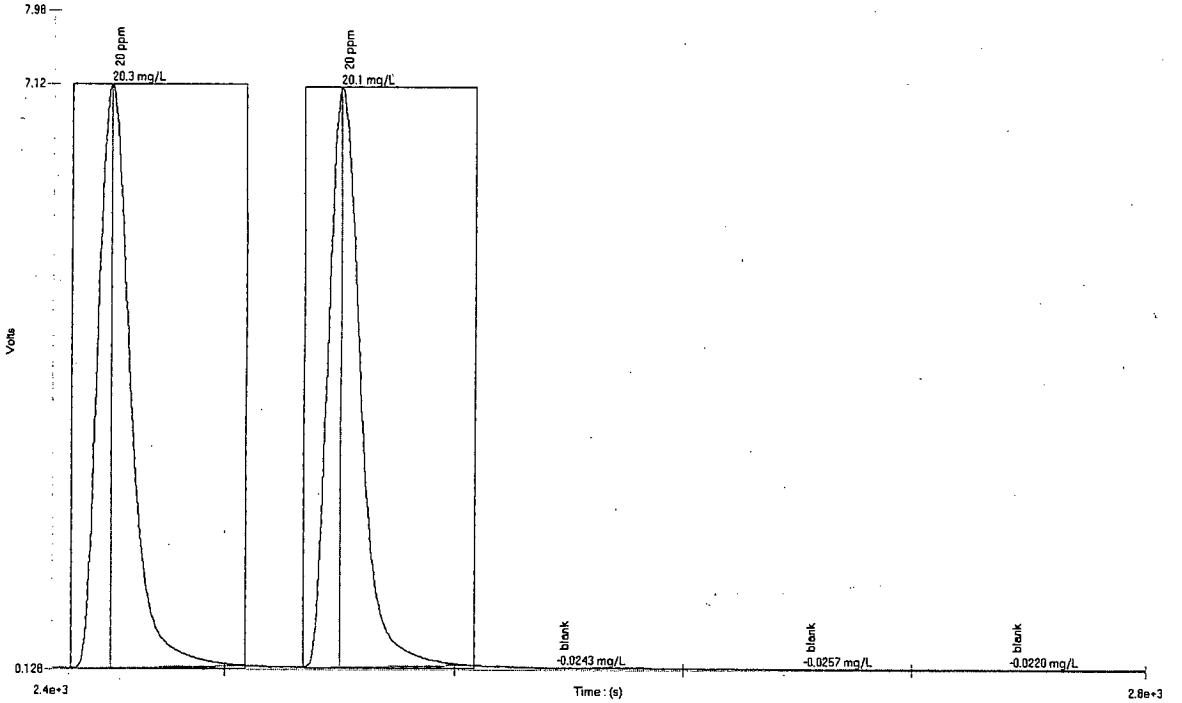
Precision Data for Nitrate/Nitrite using a 5.0 mg N/L standard

% 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

Appendix C: University of Minnesota Duluth Dr. John Pastor's Research Group - Standard Operating Procedures

Juvenile Seedling Growth Test: Oxic Conditions

Standard Operating Procedure for Test Methods using Wild Rice, *Zizania palustris*

1.1 Scope and Application

1.1.1 This method describes procedures to perform a toxicity test using wild rice in exposures of solutions containing elevated sulfate or cation concentrations under aerobic conditions.

1.1.2 This method consists of a test using a dilution series of at least four concentrations of a test chemical and a control.

1.2 Summary of Method

1.2.1 Germinated seeds of the aquatic macrophyte *Zizania palustris* are exposed in a static-renewal system to a dilution series of concentrations of sulfate or cations. The exposure duration is 10 days. The response of the germinated seeds is measured in terms of changes to growth in control plants vs. treatment as measured using biomass (weight) and measures of vegetative growth of the plant.

1.3 Quality Control Considerations

1.3.1 Toxic substances may be introduced by contaminants in dilution water, sampling hardware, or testing equipment.

1.3.2 Adverse effects of pH changes and cationic constituents in test media may augment or mask adverse effects of toxic substances.

1.3.3 Improper sampling of test solutions may adversely affect test results (see section 1.5, Standards and Reagents, and section 1.6, Toxicity Test Procedures)

1.3.4 Additional details are found in the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

1.4 Necessary Apparatus and Materials

1.4.1 Seeds of *Zizania palustris* are prepared in the laboratory for germination (see section 1.7, Wild Rice Seed Preparation). To initiate exposures of germinating seeds, sufficient numbers of conditioned seed must be available.

1.4.2 Environmental Growth Chamber: with lamps of maximum light intensity of 800 or greater μmol m^{-2} sec^{-1} (measured 6 inches below the lamps) produced by either fluorescent lamps or an LED light system and temperature control range of 15° C to 30° C ± 1°C).

1.4.3 Light meter: quantifies intensity as photosynthetic photon flux (PPF).

1.4.4 Test chambers: 70 mL Kimax (Kimble Chase Life Science and Research Products LLC) or Pyrex (Corning, Inc.) glass tubes with screw caps.

1.4.5 Meter: pH for routine physical measurements.

1.4.6 Volumetric flasks and graduated cylinders: class A, 10 – 2000 mL borosilicate glass for preparation of test solutions.

1.4.7 Volumetric pipets

1.4.8 Pipet bulbs and fillers

1.4.9 Balance: analytical, capable of accurately weighing 0.1 mg.

1.4.10 Magnetic stirrer and stir bars: for mixing test and growth media solutions

1.4.11 Filtering apparatus: for membrane and /or glass fiber filters

1.4.12 Tape: for labeling test chambers and containers for solutions

1.4.13 Water purification system: deionized water or equivalent

1.5 Standards and Reagents

1.5.1 Reagent-grade chemicals are used to prepare hydroponic growth media.

1.5.2 25 liters of a modified 1/5 strength Hoagland's stock solution (Table 1) is prepared using a ½ strength stock solution daily or more often as needed from 1.0 M stock solutions.

1.5.3 Stock SO_4 solution (3.200 g/L) is prepared daily as needed by adding 4.73 g anhydrous Na_2SO_4 (Fisher S421) or 8.22 g $MgSO_4*7H_2O$ (Fisher M63) to 800 mL deionized water and filling to 1 liter. Mixtures of Na_2SO_4 and $MgSO_4$ are determined by solving 2 equations with known Mg:Na ratios and known SO_4 final concentration.

1.5.4 Reagent water: defined as deionized water that does not contain substances that are toxic to the test organisms.

1.5.5 Appropriate amounts of each test solution (70 mL times number of replicates plus extra for analysis sample, i.e. 1600 mL for 20 replicates and ~200 mL sample) are made up immediately before use. Pre-determined amounts of 1/5 strength Hoagland's, PIPES buffer (Piperazine-N,N'-bis(2-ethanesulfonic acid) sesquisodium salt, Fisher Scientific/Acros Organics # AC32778-5000) , N, and P stock solution, and SO_4 stock solution are mixed and made to volume. The pH is adjusted to 6.8 +/- 0.2 with 1 M HCl.

Table 1. Composition of 1/5 Hoagland's Solution

Compound	Molar concentration in 1/5th strength growth solution
MgCl	0.4 mM
$CaCl_2 \cdot 2\ H_2O$	2 .0 mM
KCl	1.0 mM
NH_4Cl	0.08 mM
NaNO3	0.08 mM
KH_2PO_4	0.026 mM
H_3BO_3	22.5 µM
$MnCl \cdot 4\ H_2O$	4.5 µM
$ZnSO_4 \cdot 7\ H_2O$	0.5 µM
$CuSO_4 \cdot 5\ H_2O$	0.15 µM
MoO_3	0.07µM
Fe-EDTA	45.0 µM
$Na_2SiO_3*9H_2O$	1.5 mM
PIPES buffer	5.0 mM

1.6 Toxicity Test Procedures: Toxicant Exposures

1.6.1 Twenty 70 mL Kimax tubes are used for each test concentration prepared. Each tube is considered a replicate for the corresponding test concentration.

1.6.2 Each toxicity test will consist of at least four test concentrations of the toxicant (e.g., sodium sulfate) and a control (hydroponics medium).

1.6.3 Germinated wild rice seed (sprout) as described in section 1.7, Wild Rice Seed Preparation, are used to initiate the toxicity test.

1.6.4 Each Kimax tube is labeled with tape using a unique descriptor for the particular concentration of test solution and replicate for that tube. Each tube also is numbered from 1 to 120 and a table of these integers (1 – 120) randomized is prepared.

1.6.5 Each labeled tube is filled to the top with the particular solution as identified on its label.

1.6.6 Germinated seeds (sprouts) are removed from the pool of initial seeds (see section 1.8, Test Organisms) using a light forceps and put into the tube corresponding to the first integer read from the random integer table. This is done for all test tubes prepared for testing.

1.6.7. The filled tubes (solution and seed) are placed into every other opening in holding racks so that light can penetrate to all sides of each tube. A total of six 40-tube racks, each containing 20 tubes, are used to hold the test tubes. See Image 1.

1.6.8 Screw caps are placed loosely on the tubes.

1.6.9 All racks are placed in the growth chamber so that the spaces between the racks are the same as the spaces within the racks and the tops of the tubes are within 30 cm of the bottom of the lights. The location of each rack in the growth chamber remains the same for the test duration.

1.6.10 Test solutions in the tubes are renewed every two (2) days.

1.6.11 Solution renewals are accomplished by gently decanting or siphoning off the old solution leaving approximately one vertical cm of solution in the tube bottom. See Image 2.

1.6.12 New solutions are added by gently pouring into the tube until it reaches the top of the tube. The screw cap is then replaced on the tube.

1.6.13 Old solutions are retained for chemistry as described in the section 1.12, Analytical Chemistry.

1.6.14 Duration of the exposure is 10 days.

1.7 Wild Rice Seed Preparation

Wild rice seed must undergo a conditioning phase following its harvest from the field. In the wild, wild rice drops into the water after the seed has ripened, and sinks to the sediment. This seed, if left undisturbed, stays on or just below the surface of the sediment over the winter. This cold phase serves to condition the seed to enable it to germinate once water temperatures increase in the spring.

1.7.1 The following is a procedure that describes the method and handling of wild rice seed from initial harvest to its use in juvenile seedling toxicity tests.

1.7.2 Freshly harvested seed should be kept cool and moist and be placed into storage as soon as possible after field collection.

1.7.3 Harvested seed prepared for storage can be kept a) in plastic zip lock bags in a cooler set at just above freezing (4° C), or b) submerged in water just above freezing in the dark. Seed stored in either manner can have satisfactory germination rates for one to two years.

1.7.4 To begin the seed conditioning for germination, an aliquot of seed (approximately 2000 seeds) is removed from this ‘dry’ cold storage (as described in option (a) in 1.7.3) and placed into a container with water kept submerged at near freezing temperatures for at least one month. Following this time period, seed is ready (or conditioned) for germination for at least several months. For purposes of use in

laboratory testing, seed set in this conditioning phase is kept for up to two months before a fresh aliquot of seed is brought into the conditioning phase. Use of storage option (b) keeps the seed in this wet, cold conditioned phase until needed for testing. See Image 3.

1.8 Test Organisms, Germinated Wild Rice Seed

1.8.1 As seed is needed for testing, a smaller aliquot from the wet-stored (conditioned seed) is removed and placed into a container with water and placed in the dark incubator at 20+/- 1C. Germination tests (see Germination Growth Tests: Oxic Conditions) are initiated using this conditioned seed and placed immediately from the cold, submerged condition onto an open tray (see Image 3) to be placed into the test chambers. Seed used for initiating a toxicity test is visually screened for viability based on the color of the seed coat and fullness of the seed body. Seeds that float, are misshaped, or are otherwise malformed are not used for testing.

1.8.2 For this method, the seed will begin to sprout in about 2 to 3 days. Germinated seeds (referred to as a sprout) are selected with 1-2 cm of mesocotyl growth. A germinated seed (sprout) is described as growth of the mesocotyl that is longer than the seed coat. See Image 4.

1.8.3 Sprouts are selected from the pool of available seeds and placed into a separate container with water. A total of 150 sprouts are selected with 120 sprouts used for initiating the toxicity tests, and 20 sprouts put aside to be dried and weighed to measure initial weight.

1.9 Light, Photoperiod, Temperature and Humidity Test Conditions

1.9.1 Tests are performed under a 16h:8h light:dark schedule.

1.9.2 Light intensity is 350 µmol m^{-2} sec^{-1} as measured at the mid-point of the exposure tube.

1.9.3 Temperature is maintained at 21^{o} C during lighted periods and 19^{o} C during dark period.

1.9.4 Test growth chamber is maintained at 85% humidity.

1.10 Phytotoxic Effects

1.10.1 Observations of sprouts should be made during test solution renewal every 2 days. All abnormalities should be recorded.

1.10.2 Observations should include the date, time, treatment level, and replicate number.

1.10.3 After the duration of the test, exposure tubes are kept in the random order as placed initially.

1.1.4 Solutions are decanted into labeled sample bottles in the same manner as described for solution renewal.

1.10.5 Once the solution is removed, the sprout is removed from the tube for subsequent measurements. The sprout has three distinct sections: stem/leaf, root and seed. See Image 5.

1.10.6 Measures of stem/leaf length (mesocotyl growth) is performed by placing the stem/leaf stretched out on a flat surface next to ruler with the zero mark aligned with the point of stem-root transition. The length from the stem-root transition to the tip of the stem/leaf is measured and recorded to the nearest millimeter. See Image 6.

1.10.7 The stem/leaf growth is cut from the plant at the point of the stem-root transition and placed into pre-weighed drying tin. See Image 7.

1.10.8 Plant biomass is measured as follows: Each seedling is placed into a numbered, weighed aluminum weighing dish (Fisher 08-732-101). The dishes are placed on trays, and the trays are put into a drying oven at 100° C for at least 48 hours. Each dry sample and dish is placed into a desiccator until room temperature, and is weighed to the nearest 0.1 mg.

1.10.9 Roots are separated from the remaining seed material, placed in a labeled plastic bag and refrigerated. See Image 8.

1.10.10 The remaining seed material is placed into a pre-weighed drying pan.

1.10.11 Pans containing stem/leaf, and seed material are placed in the drying oven at 100^{o} C for at least 48 hrs.

1.10.12 Length and area of root material is determined using a flatbed scanner and imaging software using the method titled: Determination of Wild Rice Total Root Length Using Scanning Hardware and Software found in Appendix C of the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

1.10.13 After all root samples are scanned, each root sample is removed from its storage bag and placed into separate pre-weighed pans and dried for at least at 100^{o} C for at least 48 hrs.

1.10.14 All dried plant materials are weighed on a Sartorius 2700 balance to 0.1 mg following the method titled "Total Plant Biomass (Dry Weight) Methods" found in Appendix C of the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan". See Image 9.

1.11 Acceptability of Test Results

1.11.1 At least 90% of control juvenile seedlings are living at test termination.

1.11.2 Mesocotyl length of juvenile seedlings from control exposures will be at least 5.0 cm at the end of the 10 d duration of growth.

1.1.3 Control juvenile seedlings should not indicate any visible phytotoxic or developmental symptoms at any time during the test.

1.12 Analytical Chemistry

1.12.1 Sampling and analysis of chemical solutions used for initiating and renewing test exposures will use the following procedures.

1.12.2 New test solutions –Immediately after adding the new test solution into the jars an aliquot (approximately 250 ml) of the remaining unused portion is poured directly into a pre-labeled sample bottle.

1.12.3 Old test solutions – When exchanging solution or before decanting the final solution the Kimax tube is inverted once to mix the solution and is poured directly into a pre-labeled sample bottle. Depending on the analyses required, it may be necessary to make a composite of the solution in multiple replicate tubes from a given treatment.

1.12.4 Sulfate concentration is measured following the method titled, "Determination of Sulfate By Flow Injection Analysis" found in Appendix C of the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

References

U.S. EPA. 2012. Ecological Effects Test Guidelines. OCSPP 850.4230: Early Seedling Growth Toxicity Test. EPA 712-C-010.

U.S. EPA. 2012. Ecological Effects Test Guidelines. OCSPP 850.4100: Seedling Emergence and Seedling Growth. EPA 712-C-012.

U.S. EPA 2012. Ecological Effects Test Guidelines. OCSPP 850.4400: Aquatic Plant Toxicity Test Using *Lemna* spp. EPA 712-C-008.

U.S. EPA. 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th ed. EPA-821-R-02-013.

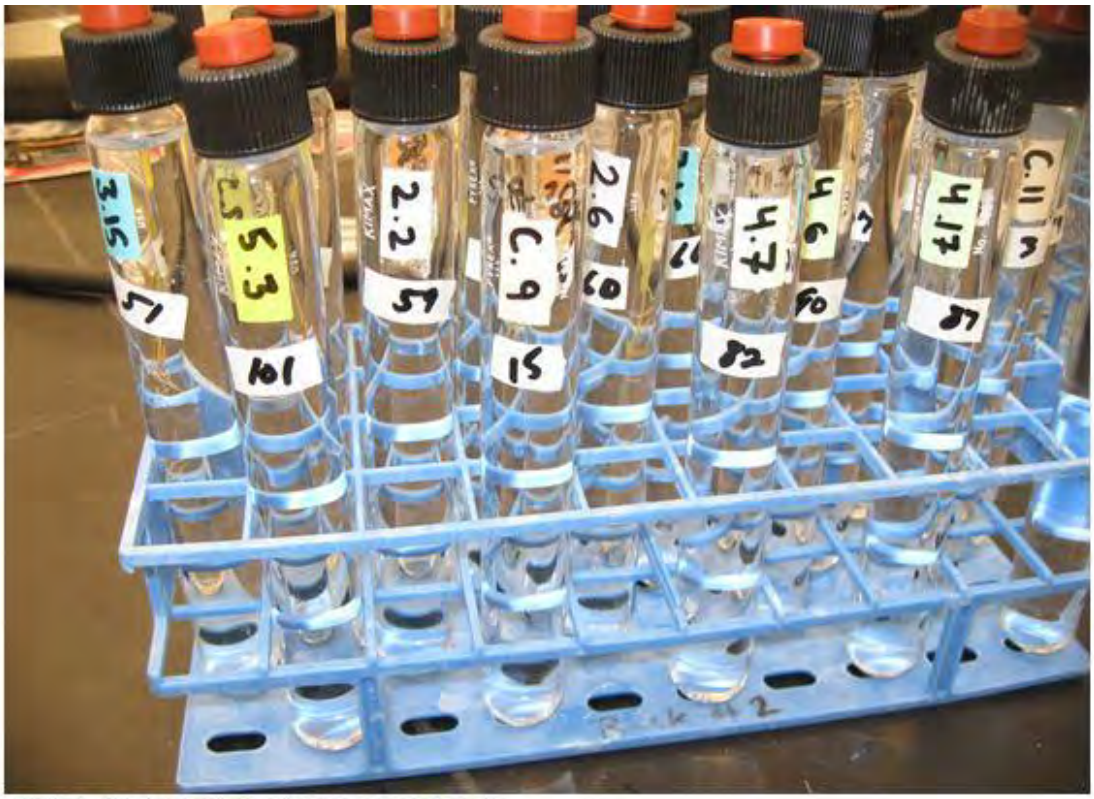


Image 1. Random placement of exposure tubes


Image2. Exposure solution renewal

Image3. Wild rice seed conditioned for germination.

Image 4. Wild rice sprout selection; sprouts on the left have mesocotyl growth of 1-2 mm long, sprouts on the right have mesocotyl growth either too long or too short to be acceptable for test initiation.

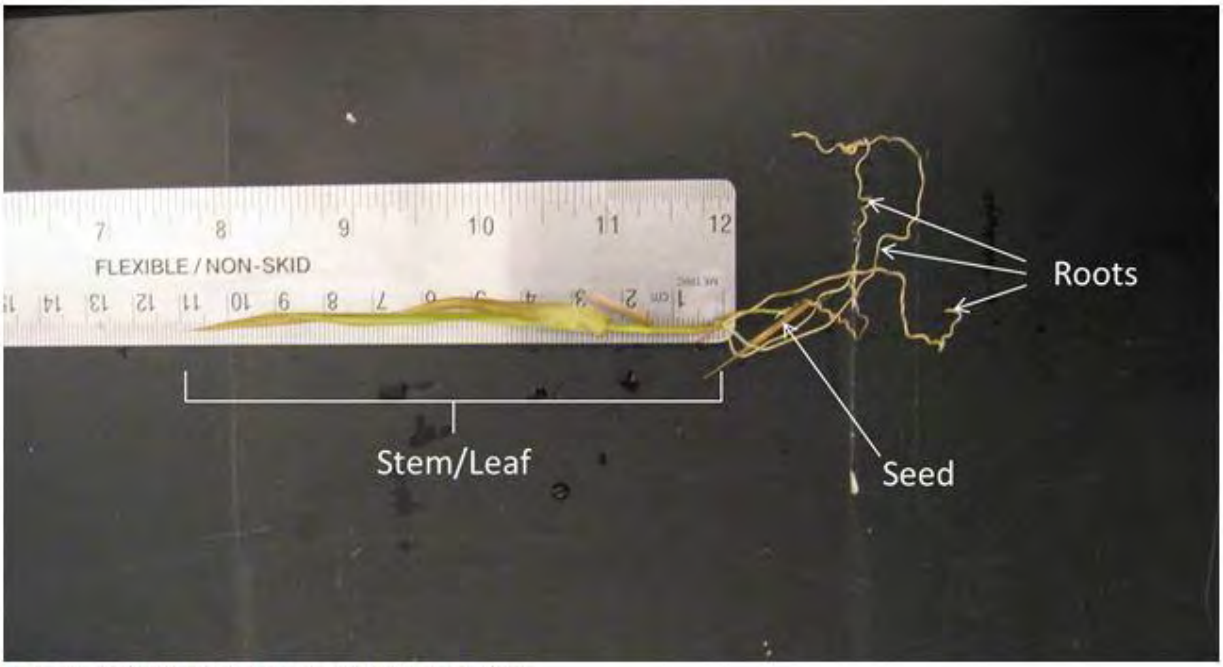


Image 5. Identification of sections of wild rice sprout.

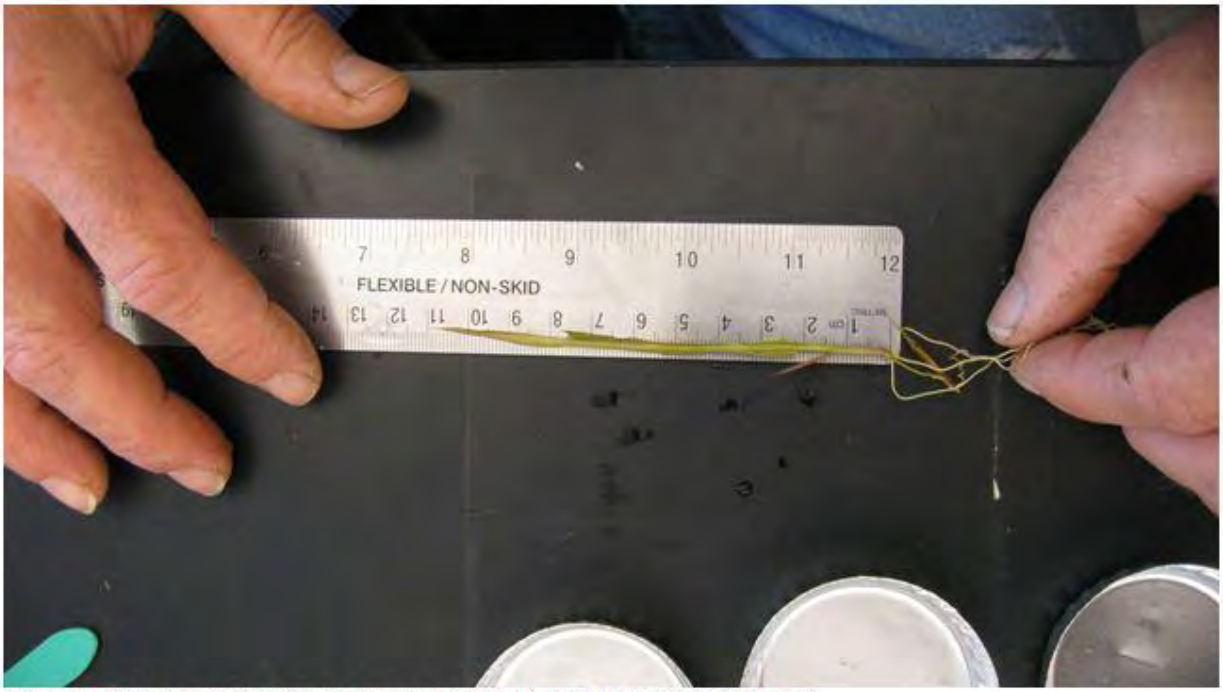


Image 6. Wild rice seedling length measurement following 10 d exposure period.

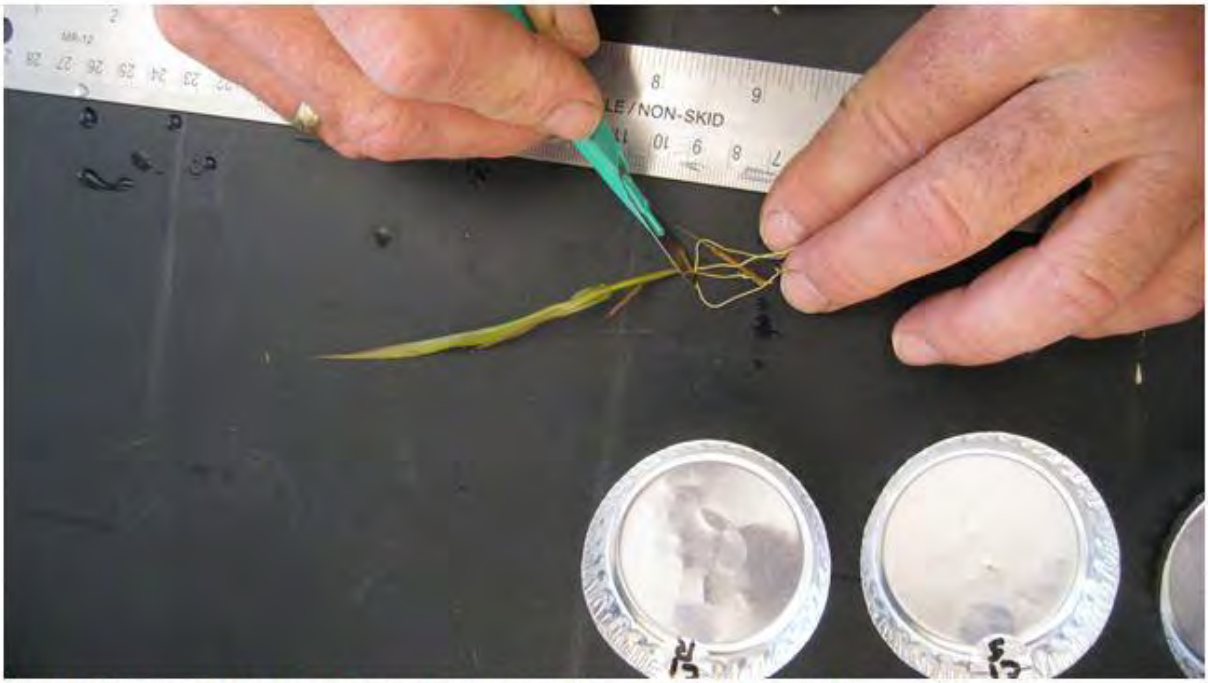


Image 7. Wild rice seedling showing removal of stem portion in preparation for drying.

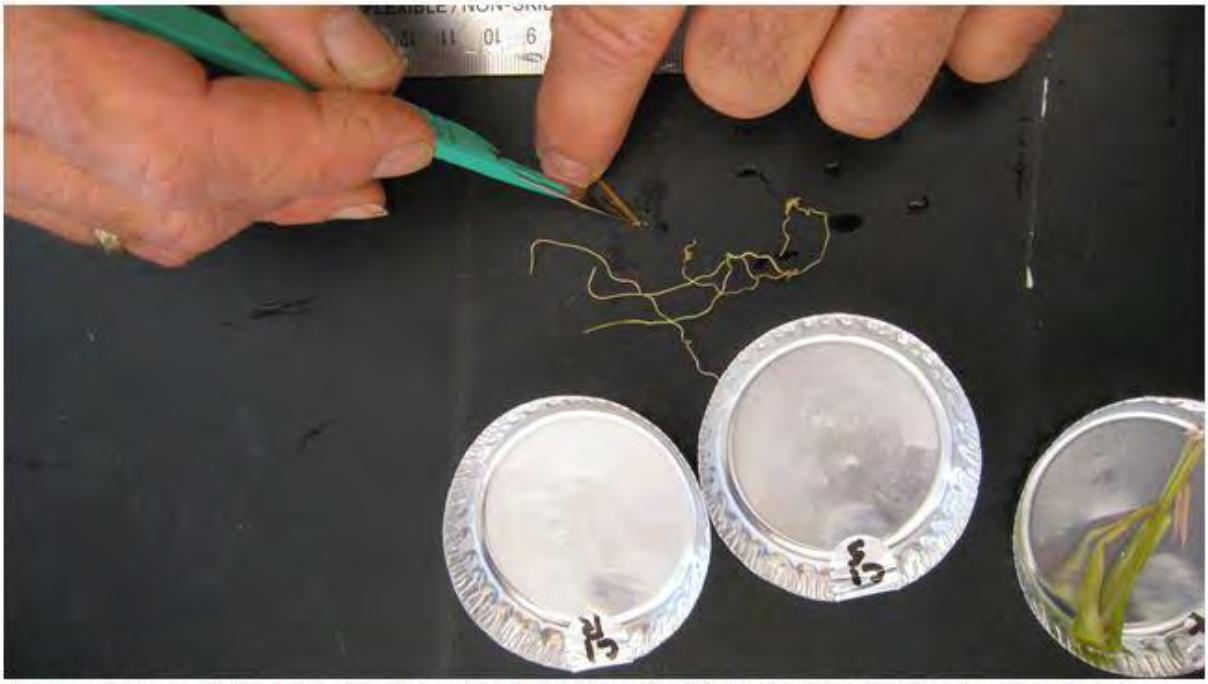


Image 8. Wild rice seedling root removal showing roots being cut from remaining seed material in preparation for measuring root length and area; stem portion of seedling is shown in a drying pan.

Image 9. Wild rice seedling showing stem, root and remaining seed portions in preparation for drying.

Germination Growth Test: Oxic Conditions

Standard Operating Procedure for Test Methods using Wild Rice, *Zizania palustris*

1.1 Scope and Application

1.1.1 This method describes procedures to perform a toxicity test using wild rice in exposures of solutions containing elevated sulfate or cation concentrations under aerobic conditions.

1.1.2 This method consists of a test using a dilution series of at least four concentrations of a test chemical and a control.

1.2 Summary of Method

1.2.1 Seeds of the aquatic macrophyte *Zizania palustris* are conditioned for germination and exposed in a static- renewal system to a dilution series of concentrations of sulfate or cations. The exposure duration is 10 days. The response of the germinating seeds is measured in terms of changes to germination rate and growth in control plants vs. treatment.

1.3 Quality Control Considerations

1.3.1 Toxic substances may be introduced by contaminants in dilution water, sampling hardware, or testing equipment.

1.3.2 Adverse effects of pH changes and cationic constituents in test media may augment or mask adverse effects of toxic substances.

1.3.3 Improper sampling of test solutions may adversely affect test results (see section 1.5 on Standards and Reagents and section 1.6 on Toxicity Test Procedures)

1.3.4 Additional details are found in the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

1.4 Necessary Apparatus and Materials

1.4.1 Seeds of *Zizania palustris* are prepared in the laboratory for germination (see section 1.7 on wild rice seed preparation). To initiate exposures, sufficient numbers of conditioned seed must be available. Each exposure jar contains 50 conditioned seeds.

1.4.2 Environmental Growth Chamber: Temperature control range of 15° C to 30° C ± 1°C). Germination growth tests are performed in the dark.

1.4.3 Test chambers: One pint (470 mL) glass jars with lids.

1.4.4 Meter: pH for routine physical measurements.

1.4.5 Volumetric flasks and graduated cylinders: class A, 10 – 2000 mL borosilicate glass for preparation of test solutions.

1.4.6 Volumetric pipets

1.4.7 Pipet bulbs and fillers

1.4.8 Balance: analytical, capable of accurately weighing 0.1 mg.

1.4.9 Magnetic stirrer and stir bars: for mixing test and growth media solutions.

1.4.10 Filtering apparatus: for membrane and /or glass fiber filters.

1.4.11 Tape: for labeling test chambers and containers for solutions.

1.4.12 Water purification system: deionized water or equivalent.

1.5 Standards and Reagents

1.5.1 Reagent-grade chemicals are used to prepare hydroponic growth media.

1.5.2 25 liters of a modified 1/5 strength Hoagland's stock solution (Table 1) is prepared using a ½ strength stock solution daily or more often as needed from 1.0 M stock solutions.

1.5.3 Stock SO_4 solution (3.200 g/L) is prepared daily as needed by adding 4.73 g anhydrous Na_2SO_4 (Fisher S421) or 8.22 g $MgSO_4*7H_2O$ (Fisher M63) to 800 mL deionized water and filling to 1 liter. Mixtures of Na_2SO_4 and $MgSO_4$ are determined by solving 2 equations with known Mg:Na ratios and known SO_4 final concentration.

1.5.4 Reagent water: defined as deionized water that does not contain substances that are toxic to the test organisms.

1.5.5 Appropriate amounts of each test solution (one pint (approximately 400 mL) times number of replicates plus extra for analysis sample, i.e. 1400 mL for 3 replicates and ~200 mL sample) are made up immediately before use. Pre-determined amounts of 1/5 strength Hoagland's, PIPES buffer (Piperazine-N,N'-bis(2-ethanesulfonic acid) sesquisodium salt, Fisher Scientific/Acros Organics # AC32778-5000) , N, and P stock solution, and SO_4 stock solution are mixed and made to volume. The pH is adjusted to 6.8 +/- 0.2 with 1 M HCl.

Table 1. Composition of 1/5 Hoagland's Solution

Compound	Molar concentration in 1/5th strength growth solution
MgCl	0.4 mM
$CaCl_2 \cdot 2\ H_2O$	2 .0 mM
KCl	1.0 mM
NH_4Cl	0.08 mM
NaNO3	0.08 mM
KH_2PO_4	0.026 mM
H_3BO_3	22.5 µM
$MnCl \cdot 4\ H_2O$	4.5 µM
$ZnSO_4 \cdot 7\ H_2O$	0.5 µM
$CuSO_4 \cdot 5\ H_2O$	0.15 µM
MoO_3	0.07µM
Fe-EDTA	45.0 µM
$Na_2SiO_3*9H_2O$	1.5 mM
PIPES buffer	5.0 mM

1.6 Toxicity Test Procedures: Toxicant Exposures

1.6.1 Each toxicity test will consist of at least four test concentrations of the toxicant (e.g., sodium sulfate) and a control (hydroponics medium).

1.6.2 Each test concentration and control exposure solution is replicated using three - one pint glass jars.

1.6.3 Conditioned wild rice seed as described in section 1.7, Wild Rice Seed Preparation, are used to initiate the toxicity test.

1.6.4 Each jar is labeled with tape using a unique descriptor for the particular concentration of test solution and replicate for that jar. Each jar also is numbered from 1 to 18 and a table of these integers (1 – 18) randomized is prepared.

1.6.5 Each labeled jar is filled to close to the top with the particular solution as identified on its label.

1.6.6 Conditioned seeds (50) are removed from the pool of initial seeds (section 1.8, Test Organisms) using a light forceps and put into the jar corresponding to the first integer read from the random integer table. This is done for all jars prepared for testing.

1.6.7. The jars (solution and seed) are placed onto a tray.

1.6.8 Screw caps are placed loosely on the jars.

1.6.9 The tray of jars is placed in the growth chamber and covered with aluminum foil to exclude light.

1.6.10 Test solutions in the jars are renewed every two (2) days.

1.6.11 Solution renewals are accomplished by gently decanting or siphoning off the old solution leaving approximately one vertical cm of solution in the jar bottom.

1.6.12 New solutions are added by gently pouring into the jar until it reaches the top of the jar. The screw cap is then replaced on the jar.

1.6.13 Old solutions are retained for chemistry as described in the section 1.12, Analytical Chemistry.

1.6.14 Duration of the exposure is 10 days.

1.7 Wild Rice Seed Preparation

Wild rice seed must undergo a conditioning phase following its harvest from the field. In the wild, wild rice drops into the water after the seed has ripened, and sinks to the sediment. This seed, if left undisturbed, stays on or just below the surface of the sediment over the winter. This cold phase serves to condition the seed to enable it to germinate once water temperatures increase in the spring.

1.7.1 The following is a procedure that describes the method and handling of wild rice seed from initial harvest to its use in the germination growth toxicity tests.

1.7.2 Freshly harvested seed should be kept cool and moist and be placed into storage as soon as possible after field collection.

1.7.3 Harvested seed prepared for storage can be kept a) in air tight bags in a cooler set at just above freezing (4° C), or b) submerged in water just above freezing in the dark. Seed stored in either manner can have satisfactory germination rates for one to two years.

1.7.4 To begin the seed conditioning for germination, an aliquot of seed (approximately 2000 seeds) is removed from this ‘dry’ cold storage (as described in option (a) in 1.7.3) and placed into a container with water kept submerged at near freezing temperatures for at least one month. Following this time period, seed is ready (or conditioned) for germination for at least several months. For purposes of use in laboratory testing, seed set in this conditioning phase is kept for up to two months before a fresh aliquot of seed is brought into the conditioning phase. Use of storage option (b) keeps the seed in this wet, cold conditioned phase until needed for testing.

Germination Growth Test: Oxic Conditions

Standard Operating Procedure for Test Methods using Wild Rice, *Zizania palustris*

1.1 Scope and Application

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1.1.2 This method consists of a test using a dilution series of at least four concentrations of a test chemical and a control.

1.2 Summary of Method

1.2.1 Seeds of the aquatic macrophyte *Zizania palustris* are conditioned for germination and exposed in a static- renewal system to a dilution series of concentrations of sulfate or cations. The exposure duration is 10 days. The response of the germinating seeds is measured in terms of changes to germination rate and growth in control plants vs. treatment.

1.3 Quality Control Considerations

1.3.1 Toxic substances may be introduced by contaminants in dilution water, sampling hardware, or testing equipment.

1.3.2 Adverse effects of pH changes and cationic constituents in test media may augment or mask adverse effects of toxic substances.

1.3.3 Improper sampling of test solutions may adversely affect test results (see section 1.5 on Standards and Reagents and section 1.6 on Toxicity Test Procedures)

1.3.4 Additional details are found in the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

1.4 Necessary Apparatus and Materials

1.4.1 Seeds of *Zizania palustris* are prepared in the laboratory for germination (see section 1.7 on wild rice seed preparation). To initiate exposures, sufficient numbers of conditioned seed must be available. Each exposure jar contains 50 conditioned seeds.

1.4.2 Environmental Growth Chamber: Temperature control range of 15° C to 30° C ± 1°C). Germination growth tests are performed in the dark.

1.4.3 Test chambers: One pint (470 mL) glass jars with lids.

1.4.4 Meter: pH for routine physical measurements.

1.11 Acceptability of Test Results

1.11.1 At least 90% of germinated seeds in control jars are living at test termination.

1.11.2 Mesocotyl length of germinated seeds from control exposures will be at least 2.0 cm at the end of the 10 d duration of growth.

1.1.3 Control germinated seeds should not indicate any visible phytotoxic or developmental symptoms at any time during the test.

1.12 Analytical Chemistry

1.12.1 Sampling and analysis of chemical solutions used for initiating and renewing test exposures will use the following procedures.

1.12.2 New test solutions –Immediately after adding the new test solution into the jars an aliquot (approximately 250 ml) of the remaining unused portion is poured directly into a pre-labeled sample bottle.

1.12.3 Old test solutions – When exchanging solution or before decanting the final solution the jar is swirled to mix the solution and is poured directly into a pre-labeled sample bottle.

1.12.4 Sulfate concentration is measured following the method titled, "Determination of Sulfate by Flow Injection Analysis" found in Appendix C of the document titled: "Hydroponic Experiment on Response of Wild Rice to Sulfate - Quality Assurance Project Plan"

References

U.S. EPA. 2012. Ecological Effects Test Guidelines. OCSPP 850.4230: Early Seedling Growth Toxicity Test. EPA 712-C-010.

U.S. EPA. 2012. Ecological Effects Test Guidelines. OCSPP 850.4100: Seedling Emergence and Seedling Growth. EPA 712-C-012.

U.S. EPA 2012. Ecological Effects Test Guidelines. OCSPP 850.4400: Aquatic Plant Toxicity Test Using *Lemna* spp. EPA 712-C-008.

U.S. EPA. 2002. Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, 4th ed. EPA-821-R-02-013.

Image 1. Examples of conditioned seeds used for initiating germination growth tests.

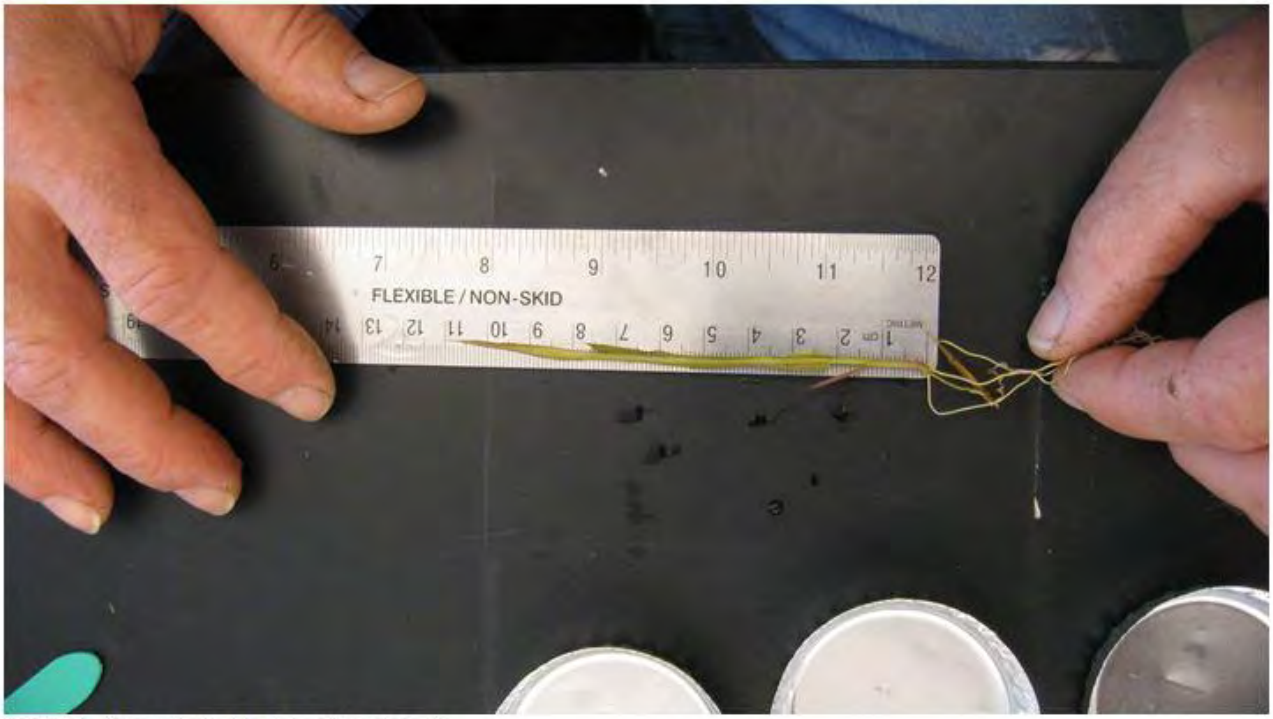

Image 2. Measurement of seedling length.

DETERMINATION OF SULFATE BY FLOW INJECTION ANALYSIS

(TURBIDIMETRIC METHOD)

Brad Dewey and John Pastor

University of Minnesota Duluth

Date: June 17, 2013

DETERMINATION OF SULFATE BY FLOW INJECTION ANALYSIS

1. SCOPE AND APPLICATION

1.1. This method covers the determination of sulfate in aqueous lab samples, ground and surface waters. If the sample is filtered through a 0.45 micron pore size filter, the result is termed dissolved sulfate.

1.2. The applicable range is 3 to 100 mg SO_4/L. The method detection limit is 0.95 mg SO_4/L as determined in our laboratory.

1.3. The method throughput is 52 injections per hour.

2. SUMMARY OF METHOD

2.1. Sulfate in the sample is precipitated with barium chloride. The precipitate scatters light at 420 nm to produce a signal proportional to sulfate concentration. The precipitate is suspended as a colloid with gelatin and polyvinyl alcohol.

3. INTERFERENCES

3.1. Color and suspended particulates will interfere.

3.2. Silicate in excess of 500 mg SiO_2/L and large quantities of organic matter interfere.

3.3. Sulfites and sulfides may oxidize and then precipitate as barium sulfate.

4. SAFETY

4.1. 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.

4.2. The 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.

4.3. MSDS for all chemicals are at hand in the lab. The reagent waste stream from the autoanalyzer is collected and disposed of through the UMD Hazardous Waste Management Program.

4.4. The following chemicals have the potential to be highly toxic or hazardous. For detailed explanations, consult the MSDS.

4.4.1. Hydrochloric acid

4.4.2. Barium Chloride

4.4.3. Poly (vinyl alcohol)

5. EQUIPMENT AND SUPPLIES

5.1. Sartorius 2700 balance capable of accurately weighing to the nearest 0.0001 g.
5.2. Mettler PE3600 balance capable of weighing to the nearest 0.01g.
5.3. Class A volumetric flask to make primary standard.
5.4. Eppendorf Reference 100-1000 uL pipettor used to make up calibration standards.
5.5. Samples are stored in plastic bottles.
5.6. Lachat Quik Chem 8000 flow injection autoanalyzer designed to deliver and react sample and reagents in the required order and ratios.
  5.6.1. Lachat Random Access Sampler.
  5.6.2. Lachat Multichannel Proportioning Pump.
  5.6.3. Lachat QuikChem Sulfate Manifold.
  5.6.4. Lachat QuikChem 8000 Automated Ion Analyzer.
  5.6.5. Lachat Omnion Data System (Version 3.0.220.04 FIA software).

6. REAGENTS AND STANDARDS

6.1. PREPARATION OF REAGENTS

Lab reagent and calibration standard water source is a Millipore Milli-Q Academic system, fed from a reverse osmosis system.

Reagent 1. Stock Hydrochloric Acid Solution, 6M

By Volume: To a **100 mL** volumetric flask containing **40 ml** of **water**, add **50 mL conc. hydrochloric acid** (HCl). Dilute to the mark and invert to mix.

Reagent 2. Working Hydrochloric Acid, 0.10 M

By Volume: In a **1 L** volumetric flask containing approximately **700 mL water,** add **16.7 mL of hydrochloric acid stock** (Reagent 1). Dilute to the mark and invert to mix.

Reagent 3. Barium Chloride Solution

The barium chloride reagent should be prepared the day before it is used since it must be cooled slowly to room temperature for the next day's analysis. Use the barium chloride reagent for only two days and then discard it. If the barium chloride reagent is used beyond two days, sensitivity of the method will be decreased.

In a **50 mL** beaker place **2.0 g Gelatin from Bovine Skin ~225 g bloom** (Aldrich G9382-100) **and 20 mL water**. Allow this mixture to soften for 15 minutes. The water will be completely taken up by the gelatin.

In a **250 mL** beaker suspend by stirring, **0.6 g PVA** [poly(vinyl alcohol)], 98-99% hydrolyzed, molecular weight 124,000-186,000, (Aldrich 36,316-25) in **50 mL water**. Allow to stir for at least 15 minutes. The PVA will not completely dissolve at this point.

In a **500 mL** erlenmyer flask with graduations, place about **400 mL water**. Bring to a boil using a flame, hotplate or microwave. The water should be hot enough to produce steam above the beaker. Add the PVA suspension. The PVA in the small beaker will not be completely dissolved. Transfer the dissolved and undissolved PVA to the hot water while the hot water is stirred. Add the softened gelatin to the hot water. It is not necessary to transfer these quantitatively. Continue to heat and stir until all of the solid material dissolves. This may take as long as one hour. Make the volume up to 500 mL using flask graduations.

Filter through rinsed glass wool into a 500 ml container. (The glass wool is placed in the bottom of a funnel. It is important to rinse the glass wool in the funnel with several volumes of DI water before use.) Add **25.0 g barium chloride dihydrate** ($BaCl_2$ $2H_2O$) (Aldrich 21756-500, ACS Reagent Grade) and stir to dissolve. At this point the solution should be slightly turbid. The barium chloride reagent should be allowed to cool slowly to room temperature before use.

6.2. PREPARATION OF STANDARDS

Standard 1. Stock Standard 100 mg SO_4/L

In a 1 L volumetric flask dissolve **0.1479 g anhydrous sodium sulfate** (Na_2SO_4) (Fisher S421-1 ACS Certified) that has been dried for two hours at 105° C and stored in a lab desiccator in about 800 mL of milliQ water. Dilute to the mark and invert to mix. The volumetric flask is sealed and stored at 4° C in the lab refrigerator.

Working standards are prepared daily. Approximately 50mL of Stock SO_4 standard is poured into a 100mL beaker and allowed to come to room temperature. The standards are made up in Lachat 15 mL plastic standard vials with an Eppendorf Research 100-1000uL pipette according to the following dilutions:

Std 1 - 100 mg/L = Stock solution
Std 2 - 50 mg/L = 6mL water + 6 mL Stock solution
Std 3 - 25 mg/L = 9mL water + 3 mL Stock solution
Std 4 - 10 mg/L = 9 mL water + 1 mL Stock solution
Std 5 - 5 mg/L = 9 mL water + 1 mL Std 2
Std 6 – 2.5 mg/L = 9.5 mL water + 0.5 mL Std 2
Std 7 - 0 mg/L = water blank

7. SAMPLE COLLECTION, PRESERVATION AND STORAGE

7.1. No chemical preservation is required. Cool the samples to 4^{o} C.

7.2. Samples are collected in 60 mL plastic bottles. All bottles are pre-washed with Decon Neutrad detergent, rinsed with reagent water, placed in 1N HCl acid bath, then rinsed at least twice with reagent water and allowed to dry before use.

7.3. Samples should be analyzed as soon as possible after collection. If storage is required, samples maintained at 4^{o} C may be held for up to 28 days.

8. QUALITY CONTROL

8.1. Lab batches consist of up to 20 environmental samples. A set of laboratory prepared standards standards is run before each batch with 25 mg/L check standards run after every 10 samples and at the end of a batch. The standards are fitted by the Omnion software to a 3^{rd} order polynomial calibration curve. The minimum acceptable r^2 for the calibration is 0.995. If this calibration fit is not achieved the standards are re-run and/or standards are re-made and re-run until acceptable. A Quality Control Sample (QCS) is prepared using a source different from the source routinely used to prepare the Calibration Standards. The QCS is used to verify the accuracy of the calibration curve. The reported concentrations for the QCS and for the check standards must be within +/- 5% of the "true" concentration or the standards and preceding samples are re-run. The reagent lines are flushed with alkaline EDTA solution (65 g NaOH plus 6 g disodium EDTA per liter) for several minutes after every batch analyzed to prevent deposition of BaSO4 on the flow cell walls.

8.2. The Method Detection Limit (MDL) was established at 0.95 mg/L SO4.

8.3. The Lower Reportable Limit is 2.5 mg/L SO4.

8.4. The upper detection limit is 100 mg/L SO4. Samples which are reported to be greater than 100 mg/L are run again after appropriate dilution. Samples from mesocosms with SO4 treatments greater than 100 mg/L SO4 are diluted with MilliQ water before analysis (150 mg/L SO4 treatment samples are diluted by a factor of two, 300 mg/L treatment samples are diluted by a factor of four).

8.5. On 6/20/2013, the mean and standard deviation for 10 replications of 100 mg/L standard was 100.85 +/- 1.52 (RSD = 1.51%). For 10 replications of 10 mg/L SO4 standard, the mean and standard deviation was 9.99 +/-0.28 (RSD = 2.80%).

8.6. Analyses of laboratory blanks are required to demonstrate freedom from contamination. Analyze a reagent water blank, initially, and with each analytical batch. The blank must be subjected to the same procedural steps as a sample. If analyte is detected in the blank at a concentration greater than the RL, 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.

8.7. Analysis of a Laboratory Control Sample (LCS) is required to demonstrate method accuracy in a matrix-free environment. The laboratory must spike a reagent blank water sample for each batch of up to 20 samples. The sample aliquot shall be spiked to yield a final concentration of about 25 mg/L SO_4.

8.7.1. Compute the percent recovery using the following equation:

% Recovery= ((S1-D1)/K)*100

Where S1 = the determined concentration of the analyte in the LCS sample, D1 = the determined concentration of the analyte in the method blank, and K = the actual concentration of the analyte in the spiked sample.

8.7.2. The % Recovery for the LCS shall meet the current laboratory acceptance criteria of +/- 20% of the actual concentration of the analyte in the spike. If the criteria are not met, the analytical system is judged to be out of control and the problem must be immediately corrected. After corrective action, the analytical batch is reanalyzed.

8.8. 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 laboratory must spike, in duplicate, one sample in each batch of up to 20 samples. The two sample aliquots shall be spiked to yield a final concentration of about 25 mg/L SO_4.

8.8.1. Compute the percent recovery using the following equation:

% Recovery= ((S1-D1)/K)*100

Where S1 = the determined concentration of the analyte in the MS sample, D1 = the determined concentration of the analyte in the background environmental sample, and K = the actual concentration of the analyte in the spiked sample.

The % Recovery for the MSs or MSDs shall meet the current laboratory acceptance criteria of +/- 20% of the actual concentration of the analyte in the spike. If the criteria are not met, the analytical system is judged to be out of control and the problem must be immediately corrected. After corrective action, the analytical batch is reanalyzed.

8.8.2. Compute the Relative Percent Difference using the following equation:

RPD = (((D1 – D2)*2)/(D1 + D2))*100

Where, D1 = Concentration of analyte in the sample and
D2 = Concentration of analyte in the second (duplicate) sample.

The RPD for duplicates shall meet the current laboratory acceptance criteria of ≤30%. If the criteria are not met, the analytical system is judged to be out of control and the problem must be immediately corrected. After corrective action, the analytical batch is reanalyzed.

9. PROCEDURE

9.1. SYSTEM START UP PROCEDURE:

9.1.1. Prepare reagent and standards as described in Section 6.

9.1.2. Set up manifold as described in QuikChem Method 10-116-10-1-A.

9.1.3. Input data system parameters as described in QuikChem Method 10-116-10-1-A.

9.1.4. 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.

9.1.5. Place samples and/or standards in the autosampler. Input the information required by the data system, such as concentration, replicates and QC scheme.

9.1.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the instrument responses for each standard.

9.2. SYSTEM NOTES

9.2.1. The calibration fits a third order polynomial.

10. DATA ANALYSIS AND CALCULATIONS

10.1. Calibration is done by injecting standards. A calibration curve is created by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

10.2. Report only those values that fall between the lowest and highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

10.3. Report results in mg SO_4/L.

11. WASTE MANAGEMENT

11.1. 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 operations. Compliance with all sewage discharge permits and regulations is also required.

12. REFERENCES

12.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Revised March 1983, Method 375.4

12.2. Standard Methods, For the Examination of Water and Waste Water, 14th ed. Revised 1975, Method 427C, p.496 - 498.

12.3. QuikChem Method 10-116-10-1-A, Determination of Sulfate by Flow Injection Analysis. August 28, 2003. Lachat Instruments.

13. TABLES

13.1. Data System Parameters for QuikChem 8000

The timing values listed below are approximate and will need to be optimized using graphical events programming.

Sample throughput:	52 samples/hour, 65 seconds/sample
Pump Speed:	35
Cycle Period:	65

Analyte Data:

Concentration Units:	mg SO_4/L Peak Base Width: 22 seconds
% Width Tolerance:	100
Threshold:	16000
Inject to Peak Start:	15 seconds
Chemistry:	Direct

Calibration Data:

Calibration Rep Handling:	Average
Calibration Fit Type:	3rd Order Polynomial
Weighting Method:	None
Force through zero:	No

Sampler Timing:

Min. Probe in Wash Period:	7.8 seconds
Probe in Sample Period:	20.6 seconds

Valve Timing:

Load Time:	0 seconds
Load Period:	14 seconds
Inject Period:	48 seconds

Total Plant Biomass (Dry Weight) Methods

1. Application
This method covers the procedure for measuring the total weight of plant matter.

2. Summary of Methods
Total biomass of plant matter is determined by drying a sample at 100-105°C.

4. Potential Interferences
4.1 Care must be taken to avoid loss of plant material during drying and weighing process.

5. Sample Collection, Preservation and Handling
5.1 Plant material is collected following measurements of length on fresh plant removed following the termination of toxicity test exposures.
5.2 Plant samples are placed into pre-weighed weighing pans and dried at 100-105°C.

6. Equipment and Analytical instruments
6.1 Oven (force draft or circulating) capable of constant temperature of 100-105°C ±5°.
6.2 Weighing pans (aluminum).
6.3 Scale accurate to weighing 0.1 mg.
6.4 Glass desiccator jar containing desiccant (gypsum or silica gel).

7. Consumable Supplies, Reagents and Standards
7.1 Aluminum weighing pans.

8. Procedure for Analysis
8.1 Plant matter is placed into pre-weighed weighing pans following termination of toxicity tests exposures.
8.2 Record weight of weighing pan containing the plant material to the nearest 0.1 mg.
8.3 Place weighing pan with weighed plant material in drying pan and put into drying oven for at least 48 h.
8.4 After 48 hours or when stable reading is obtained, remove weighing pan from oven. Place in desiccator to cool.
8.5 Record weight of weighing pan and dry sample to the nearest 0.1 mg.

9. Calculations
Total (%) Dry Weight = $\left[\text{(weight dry sample + weighing pan) - (weight empty weighing pan)}\right]$ X 100

10. Quality Control
10.1 Determination of stable dry weight is achieved by placing three individual weighing pans plus plant material into the desiccator jar. Once cooled, the weight of each pan is recorded, and the pans are placed back into the drying oven for one half hour. After this, the pans are removed, placed into the desiccator jar to cool and weighed once again. If the dry weight of each pan differs by less than 0.5 mg or 4%, whichever is less, the weight is stable and the weighing of all individual weighing pans with plant matter can be completed.

11. Data Reviewing and Reporting
Data are reviewed by the senior analyst for completeness and correctness before being sent out. Report results in total dry weight of plant matter.

12. References
12.1 Adapted from Standard Methods (SM2540 Solids).

DETERMINATION OF WILD RICE TOTAL ROOT LENGTH USING SCANNING HARDWARE AND SOFTWARE

(Epson Perfection 4990 Photo Scanner and WinFOLIA Software)

Dr. John Pastor and Brad Dewey

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DETERMINATION OF TOTAL ROOT LENGTH OF JUVENILE SEEDLING BY ROOT SCANNING HARDWARE AND SOFTWARE

1. SCOPE AND APPLICATION

1.1. This Standard Operating Procedure was developed as a document to support the hydroponic sulfate and sulfide toxicology studies conducted at the University of Minnesota – Duluth Biology department by Dr. John Pastor, on behalf of the MPCA Wild Rice Sulfate Standard Study. This SOP will also be included in the Hydroponic – Sulfate and Sulfide Quality Assurance Project Plan (QAPP) as an appendix.

2. SUMMARY OF METHOD

2.1. This standard operating procedure outlines the activities associated with the determination of root length of juvenile seedlings sprouted as one endpoint of the hydroponic sulfate toxicology experiment. The following sections detail: 1) Sample Collection, Preservation, and Storage Procedures. 2) Scanning Procedure 3) Quality Control Activities and 4) Data Analysis and Calculation of length procedures.

3. SAMPLE COLLECTION, PRESERVATION AND STORAGE

3.1. After the plant parts are separated, the root segments of each plant are placed in small (3 by 5 inch) plastic bags, sealed, and labeled accordingly.

3.2. The root samples are immediately placed in a lab refrigerator and stored at 4C until scanned. Holding time is up to 3 days.

3.3. Roots are returned to the appropriate plastic bag after scanning procedures are complete and the results pass the minimum quality control elements. When scanning is complete, all root samples are placed into pre-weighed tins to be dried and weighed.

4. PROCEDURES

4.1. The roots from each test plant are removed from the plastic bag and placed into a clear plastic scanning tray (approx. 8”w x 10”l x 1”d).

4.2. The roots are covered with deionized water, approximately 1cm.

4.3. The roots are positioned to minimize crossing and overlap.

4.4. The tray is covered with a flat black cover.

4.5. Root segments are scanned using an Epson Perfection 4990 photo scanner controlled by the image acquisition component of Regent Instruments, WinFOLIA software.

5. QUALITY CONTROL

5.1. The root image is observed and accepted or determined to be not acceptable (roots extending outside of scanned area, fuzzy image due to roots “drifting”, air bubbles along root surface).

5.2. Roots are scanned until an acceptable image is produced.

6. DATA ANALYSIS AND CALCULATION

6.1. Acceptable root images are saved to a designated external hard drive with the file name derived from the date, the test conducted, the sample treatment, and the replicate number.

6.2. The root images are analyzed using Regent Instruments WinRHIZO software.

6.3. The analysis parameters are set to pale root on dark background, manual pixel threshold which optimizes root recognition, and a minimum individual area of 0.05 cm^2 which removes any background debris.

6.4. The roots are analyzed and the calculated root length, and associated root parameters and the scanned image are saved to the designated external hard drive with ANZ added to the original image file name.

6.5. All original root scans will be saved on a computer hard drive until the values derived from the scans are reported elsewhere. The original root scans may then be copied to other file storage options.