# Wild Rice Sulfate Standard Sediment Incubation Experiment - Quality Assurance Project Plan

November 2013

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

Minnesota Pollution Control Agency

# Section A: Project Management Elements

## Section A.1: Approvals

**Approval:** **Date:**

12/07/2013

**Nathan Johnson, Ph.D.**
*Assistant Professor - University of Minnesota, Duluth (UMD) - Civil Engineering*
*Work Order Coordinator*
*(218)726-6435*
*nwjohnso@d.umn.edu*

10/11/2013

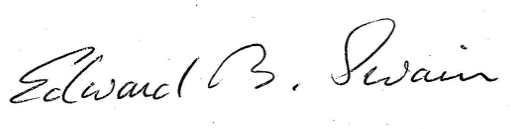
**John Pastor, Ph.D.**
*Professor - University of Minnesota, Duluth (UMD) - Biology Department*
*Principle Investigator*
*(218)726-7001*
*jpastor@d.umn.edu*

11/17/2013

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

## Section A.1: Approvals (Continued)

**Approval:** **Date:**



11/03/2013

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

11/14/2013

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

11/17/2013

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

**Approval:** **Date:**

11/07/2013

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

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

## Section A.2: Table of Contents

## Contents

## Section A.3: Distribution List

The listed individuals will receive copies of the approved Quality Assurance Project Plan (QAPP) and subsequent revisions:

Nathan Johnson Ph.D., *University of Minnesota - Duluth (UMD), (218) 726-6435*
Will DeRocher, Graduate Researcher, *University of Minnesota – Duluth (UMD) (218) 720-4294*
John Pastor Ph.D., *University of Minnesota – Duluth (UMD), (218) 724-4061*
Shannon Lotthammer, *MPCA, (651) 757-2537*
Edward Swain, Ph.D., *MPCA, (651) 757-2772*
Patricia Engelking, *MPCA, (651) 757-2340*
William Scruton, *MPCA, (651) 757-2710*
Paul Moyer, *Minnesota Department of Health (MDH), (651) 201-5669*
Jeff Brenner, *MDH, (651) 201-5353*
Shane Olund, *MDH, (651) 201-5357*
Amy Myrbo, Ph.D., *University of Minnesota - Twin Cities (UMN) and National Lacustrine Core Facility/Limnological Research Center (LacCore/LRC), (612) 626-7889*

## Section A.4: Project Organization and Responsibility

### Section A.4.1: UMD Work Order Coordinator – Nathan Johnson, Ph.D.

The UMD Work Order Coordinator will:

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

### Section A.4.2: Graduate Researcher – Will Derocher

- Review the Quality Assurance Project Plan (QAPP) including subsequent revisions.
- With guidance from the MPCA Project Manager, Work Order Coordinator, and Principle Investigator design, develop, and implement the sediment incubation experiment, maintaining project notebooks and recording data in an appropriate database.
- Critically examine all data generated for the project and annotate the data with any concerns.
- Make preliminary interpretations of the data.
- Assist the Work Order Coordinator in preparing data and reports to the MPCA that summarize the experiments, results, preliminary interpretations, and include an attachment of all final data in electronic database format.
- In coordination with the Work Order Coordinator and at their discretion, publish results from the project in a peer-reviewed journal.

### Section A.4.3: The University of Minnesota – Duluth Principal Investigator – John Pastor, Ph.D.

The Principal Investigator will:

- Review and approve the Quality Assurance Project Plan (QAPP) including subsequent revisions.
- Work in a collaborative capacity with Work Order Coordinator and Graduate Researcher to support all aspects of the experiment described within.

### Section A.4.4: The MPCA Division Manager - Shannon Lotthammer

The MPCA Division Manager will:

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

- Conduct annual performance appraisals of assigned staff specific to their position description relating to the Sulfate and Wild Rice Project.

### Section A.4.5: The MPCA Project Manager – Edward Swain, Ph.D.

The MPCA Project Manager will:

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

### Section A.4.6: The MPCA Contract Manager – Patricia Engelking

The MPCA Contract Manager will:

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

### Section A.4.6: MPCA QA Coordinator – William Scruton

The MPCA QA Coordinator will:

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

- Provide an overview to the Project Manager of analytical results and quality control data to ensure the laboratory has met Project requirements.

### Section A.4.7: MDH Inorganic Unit Supervisor – Jeff Brenner

The MDH Inorganic Unit Supervisor will:

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

### Section A.4.8: MDH Public Health Laboratory Manager – Paul Moyer

The MDH Public Health Laboratory Manager will:

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

### Section A.4.9: MDH QA Officer – Shane Olund

The MDH QA Officer will:

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

### Section A.4.10: MDH Laboratory Staff

The MDH Laboratory Staff will:

- Ensure analytical procedures are followed.
- Document the analysis and observations.
- Identify and report analytical problems to the Unit Supervisor and QA Officer.
- Manage the budget to assure that goals are met and funds and resources are responsibly allocated.
- Provide direction for the daily work activities.
- Provide technical representation at meetings.
- Prepare reports.
- Review the QAPP including subsequent revisions.

### Section A.4.11: University of Minnesota LacCore/LRC Laboratory Manager – Amy Myrbo, Ph.D.

- Ensure that the analytical requirements of the QAPP are implemented.
- Provide direct supervision and project assignment to assigned staff.
- Provide direction for the daily work activities.

- Provide technical representation at meetings.
- Provide direction for analytical requirements.
- Perform final review of analytical data reports to ensure requirements are met.
- Review and approve the QAPP including subsequent revisions.

## Section A.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 presently undertaking a study to investigate the potential effects of elevated sulfate on the growth of wild rice. One high-priority hypothesis is that the conversion of sulfate to sulfide in anoxic subsurface sediment may harm the roots of wild rice, either directly, or indirectly. Sulfide reacts with many metals, including iron, which may play a major role in controlling sulfide in the sediments of wild rice habitat. The rate at which sulfate from overlying water diffuses into and is converted to sulfide within different types of sediments (at high and low temperatures) is presently unknown. Additionally, the feasibility of maintaining environmentally relevant sulfide concentrations in laboratory experiments is also unknown. To address these issues, sediment from two different sampling sites with different characteristics will be collected and incubated at two different environmentally relevant temperatures in a laboratory setting based on an experimental design described in this document. The tasks described herein will examine depth and time dependent concentrations of sulfate, sulfide, and iron in two types of sediments and in two different temperature environments in a controlled laboratory setting. This experimental design will generate results to (a) provide a basis for comparing results from hydroponic studies to container mesocosms and field sites, (b) help identify the importance of oxygen release from wild rice roots, and (c) quantify the rate of diffusive transport of environmentally important chemicals into and out of sediment. As part of the larger Wild Rice Sulfate Standard Study, the results of this experiment, will inform and support the MPCAs decision as to whether or not a change to the existing sulfate standard is necessary to protect wild rice, and if so, what the revised standard should be. Such a change, if warranted, would be proposed in accordance with the provisions and requirements of Minnesota's Administrative Procedures Act.

## Section A.6: Project Descriptions

### Section A.6.1: Objective

The quality objectives will generally follow the guidance outlined on the Quality System webpage: (http://www.pca.state.mn.us/index.php/about-mpca/mpca-overview/agency-strategy/mpca-quality-system.html?expandable=1&menuid=&redirect=1). The Quality System for MPCA's environmental data describes the agency's general policy for data quality assurance. This QAPP falls under all requirements of the MPCA's Quality Management Plan (QMP) which is approved by U.S. Environmental Protection Agency (EPA) Region 5. The objective of this experiment is to measure, interpret, and then model, sulfide, sulfate, oxygen, and iron in the rooting environment of wild rice.

### Section A.6.2: Scope

Sediment will be collected from two wild rice environments with contrasting sediment quality and then incubated in laboratory microcosms (8 inch diameter; at least 20 vertical cm of sediment). Six microcosms will be incubated from each of two sites chosen in consultation with the MPCA Project Manager (12 microcosms total); six microcosms from one site with higher organic sediment and six microcosms from a second site with coarser, less organic, sediment. Half of each set (three from each site) will be incubated at room temperature (approximately 21 degrees C and half at approximately 4 degrees C to investigate the effects of temperature on sulfate flux and conversion to sulfide. Initially, overlying water with relatively low sulfate (similar to site water) will be maintained over sediment microcosms. Subsequently, overlying water sulfate concentrations will be increased to a concentration of 300 mg/L (consistent with concentrations discussed by permitting personnel at the MPCA) for a period of about two months. Finally, overlying water sulfate concentrations will be reduced back to ambient concentrations for a period of about two months, during which time the temperature of the 4 °C treatments may be increased to 21 °C. Flux of sulfate into (and out of) sediment will be quantified by carefully monitoring concentrations of sulfate and an inert tracer in the overlying water sulfate and by extracting sub-cores from microcosms and/or porewater with Rhizon filters at key time points (when treatments are altered). Geochemical calculations will be made to test assumptions about the chemical speciation of sulfur, iron, and other metals. The project timeline schedule is from March 25$^{th}$ 2013 to December 23$^{rd}$ 2013.

### Section A.6.3: Analytical Samples

Samples that are to be sent to the MDH Environmental Inorganic Laboratory are brought under chain of custody procedures. The samples are labeled to allow identification of each sample specific to the site where the sample was taken. Samples are labeled and identified by the type of analyses being requested. This information allows the laboratory to use the proper method when analyzing these samples and to produce identifiable records of results. Specific instructions on sampling procedures including collection, preservation and transportation, are provided in Section B.1. The lists of target analytes are provided below in Tables 1, 2 and 3. All analytical methods that are to be used are identified in these tables by the laboratory performing them, along with their location in the appendices of this document.

**Table 1: Experimental Target Analytes in Overlying Water**

| Target Analyte | Report Level (RL) | Analytical Method Reference | Laboratory | Location of Method |
|---|---|---|---|---|
| Dissolved Oxygen | 0 to 50 mg/L with 0.01 mg/L resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Conductivity | 0 to 100 mS/cm with 0.0001 unit resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| pH | 0 to 14 units with 0.001 unit resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Temperature | -5 to 50 °C with 0.01°C resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Sulfate | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Chloride | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Bromide | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Fluoride | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Dissolved Phosphate | 0.01 mg/L | QuikChem Method 10-115-01-3-E | MDH Environmental | Appendix C |
| Dissolved Nitrogen | 0.05 mg N/L | QuikChem Method 10-107-04-3-D | MDH Environmental | Appendix C |

**Table 2: Experimental Target Analytes in Porewater**

| Target Analyte | Report Level (RL) | Analytical Method Reference | Laboratory | Location of Method |
|---|---|---|---|---|
| Dissolved Oxygen | 0 to 50 mg/L with 0.01 mg/L resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Conductivity | 0 to 100 mS/cm with 0.0001 unit resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| pH | 0 to 14 units with 0.001 unit resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Temperature | -5 to 50 °C with 0.01°C resolution | Hydrolab Multiparameter Sonde | UMD Civil Engineering | Appendix D |
| Ferrous Iron | 0.75 mg/L | SM3500 Fe | UMD Civil Engineering | Appendix D |
| Sulfate | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Chloride | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Bromide | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Fluoride | 0.05 mg/L | Modified EPA 300.1 | UMD Civil Engineering | Appendix D |
| Sulfide | 0.15 mg/L | SM4500 $S^{-2}$ D | UMD Civil Engineering | Appendix D |

**Table 3: Experimental Target Analytes in Sediment**

| Target Analyte | Report Level (RL) | Analytical Method Reference | Laboratory | Location of Methods |
|---|---|---|---|---|
| Sediment - Acid Volatile Sulfide (AVS) | 0.01 mg/kg | SM4500-S2 J | MDH Environmental | Appendix C |
| ICP-MS for Extractable Metals | 0.3 ug/L | EPA 6020 A | UMD Civil Engineering | Appendix D |
| Total Sulfur | TBD | TBD | LacCore/LRC | Appendix E |
| Total Carbon | TBD | TBD | LacCore/LRC | Appendix E |
| Total Nitrogen | TBD | TBD | LacCore/LRC | Appendix E |
| Percent Solids | 0.01 mg/kg | SM4500-S2 J | MDH Environmental | Appendix C |

### Section A.6.4: Intended Data Usage

Data will be interpreted based upon the data produced, geochemical calculations and computer modeling. From this data, a simple reactive-transport model will be created and calibrated to model the rate of sulfate diffusion and transformation in sediment, as constrained by observed changes in the concentrations of sulfate and inert tracers in overlying water, porewater sulfide, AVS, and other supporting analyses. To the extent scientifically defensible, the effects of oxygen release by roots on concentrations of sulfide in sediment may be modeled.

### Section A.6.5: Technical Reports

The Work Order Coordinator will provide updates to the MPCA Wild Rice Sulfate Standard Study staff, summarizing the experiment progress and analytical data during weekly phone conversations or meetings. The Work Order Coordinator will provide a technical report to the MPCA providing and interpreting all data as well as creating a reactive-transfer model for sulfate diffusion and reaction in sediment by December 15$^{th}$, 2013.These reports will be distributed to the appropriate managers at the MPCA. The MPCA Project Team also updates management about project progress on a routine basis.

## Section A.7: Quality Assurance Objectives and Criteria

### Section A.7.1: Overview

Quality assurance objectives are developed for sampling in the sediment incubation microcosms, chain of custody, laboratory analysis and reporting (see detailed procedures in Section B.2 and B.3). Meeting these objectives will provide the MPCA with defensible information to be in the project.

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

Laboratory reports include the date of sampling, the date of analysis, the signed Chain of Custody form, a narrative of the analysis which notes items that are outside the laboratory QC limits, and the analytical results for the collected sample. In addition to the analytical results, the reports include the per cent recoveries (% R) of laboratory control sample/laboratory control sample duplicates, matrix spikes, and standard reference material and the relative per cent differences (RPD) between duplicates. Laboratory analytical QC acceptance criteria are detailed in Tables 4, 5 and 6.

#### *Section A.7.1.1: Research Directions and Decisions*

The construct and need for these temperature-dependent tests are based on a desire to better understand the potential seasonal variation in susceptibility of wild rice to sulfate exposure.

#### *Section A.7.1.2: Inputs to the Decision*

The project management team (Shannon Lotthammer, Edward Swain and Patricia Engelking) along with the Work Order Coordinator, Nathan Johnson Ph.D. and Principal Investigator, John Pastor, PhD, will be responsible for final decisions on the project. These decisions will be informed by input from MPCA permitting personnel, 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.

#### *Section A.7.1.3: Laboratory Analysis*

Due to the small volumes associated with many of the porewater samples collected in these experiments, most porewater and overlying water analyses will take place in the UMD Civil Engineering Laboratory in the labs of Drs. Johnson and Pastor. Quality assurance guidelines and SOPs for the Johnson lab are included in Appendix C. The analytes of concern from an aqueous and sedimentary medium (with Report levels and analytical methodologies) are detailed in tables 1,2 and 3 above. Due to the constraints presented by low sample volume, the MDH Inorganic Environmental laboratory will not be the lab of primary analysis, although cross checks of results between the U of M – Duluth Civil Engineering lab and MDH Inorganic Environmental lab are done frequently as a quality control activity.

### Section A.7.2 Blanks

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

### Section A.7.3: Duplicate Samples

The laboratory also prepares and analyzes duplicate samples to gain a measure of reproducibility. MPCA has a relative percent difference (RPD) goal for duplicates of 25% in waters and 50% in sediments

### Section A.7.4: Matrix Spike and Laboratory Control Samples

A laboratory may use Matrix Spike (MS) and duplicate (MSD) or Laboratory Control Sample (LCS) and duplicate (LCSD) recoveries to measure accuracy in the analyses depending on their laboratories QA/CQ procedures. Laboratory-generated limits for spike recoveries are used in validation of data (when required). Refer to the laboratory's Quality Assurance Manual (QAM) (if available) or specific analytical method located in the appendix of this QAPP for details of this QC activity.

### 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 QAM, if available.

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

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

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

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

#### *Section A.7.6.1: Accuracy*

The accuracy of the measurement is gauged through the analyses of surrogate spikes, matrix spike (MS), and/or laboratory control sample (LCS)/laboratory control sample duplicate (LCSD). Surrogate compounds are spike into every sample prior to extraction and analysis. Where possible, a MS sample is collected. If a MS cannot be analyzed, an LCS/LCSD pair may be used to measure accuracy. The percent recovery is determined by comparing the spiked sample concentration to the environmental (un-spiked) sample concentration. The formula for determining percent recovery is as follows:

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

#### *Section A.7.6.2: Representativeness*

Representativeness of the data set is the measure that expresses the degree to which the data accurately represents the population as a whole. The methods for sample collection in the laboratory, sample preservation and storage, sample preparation, and sample analysis are

reviewed to determine if appropriate procedures were followed. If the procedures as described in this QAPP were followed, sample results are considered representative of the site.

### *Section A.7.6.3: Comparability*

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

### *Section A.7.6.4: Completeness*

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

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

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

## Section A.8: Specialized Training/Certifications

### Section A.8.1: Laboratory

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

## Section A.9: Record Keeping

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

# Section B: Data Generation and Acquisition

## Section B.1: Experimental Design and Sampling Process Design

***Field Collection of Sediment***

Approximately the top 10cm of sediment was collected through the ice using a modified screen shovel. Approximately 90 liters of bulk, wet mud was collected from each site: North Bay in the St. Louis River (1/19/13, 46 39.1731N, -92 14.2168W), and the Partridge River (1/18/13, 47 31.2705N, -92 11.4350W) just upstream from Second Creek. Fifty liters of water was also collected through the ice prior to disturbing the sediment. Replicate 2.5 ” diameter cores were collected from each site with a piston corer in order to characterize in-situ physical and geochemical conditions. All mud, core, and water samples were transported back to UMD and stored at 5.5 °C until the initiation of experiments.

***Lab Sample Analysis of Initial (In-Situ) Cores***

Field collected 2.5 ” cores were immediately (within 24 hours) sectioned into 6 depth intervals (0-1 cm, 1-2 cm, 2-4 cm, 4-6 cm, 6-10 cm, 10-15 cm) and replicate cores were composited into 500 mL plastic sample jars. Composite (2 or 3 cores) sections from each site were immediately (within 20 minutes) placed into an oxygen-free (95 % N2, 5 %H2) atmosphere after measuring pH with a glass pH electrode. Samples were homogenized in the oxygen-free atmosphere and a representative subsample was removed to measure water content (as an estimate of porosity). Rhizon filters (0.2 um polyethersulfone) were used to collect approximately 35 mL of water from composite sections into polypropylene syringes. The filters/syringes were left overnight to collect sample and filled completely. A quantitative volume (~10 mL, by mass) of filtered water sample was transferred into 20 mL glass serum bottles preloaded with Zinc Acetate (20 uL of 1 M ZnAc) and Sodium Hydroxide (100 uL of 0.6 N NaOH) in the oxygen-free atmosphere for sulfide analysis. Of the remaining filtered pore water, 2.5 mL was used to quantify ferrous iron (phenanthroline method), and 10-15 mL was stored at 4 °C until analysis for sulfate and other anions by Ion Chromatography.

***Microcosm Preparation***

Sediment handling: Within 3 weeks of collection, bulk sediments from each site were composited while attempting to minimize oxidation. Large plant material (>3 ” length, >2 mm diameter) was removed by pouring aliquots of the material into a plastic bin, picking any large articles by hand then gently raking with a garden rake to remove smaller plant material and begin to homogenize the sediment. The final mixing was completed by compositing all material from a site into a rubber garbage can and using a paint mixer attached to an electric drill at low RPM to gently fold the sediment over itself to provide a thorough yet temperate blending.

***Microcosm Construction***

Custom fabricated microcosms consisted of either polycarbonate or acrylic rigid 8" I.D. tubing with a polypropylene bottom cap with either Buna-N or silicone O-rings for sealing. Silicone caulk (100% silicone) was used to ensure a thorough seal between the bottom plate and the rigid tubing. Vinyl (Scotch Super 88) electrical tape was used as a final barrier between the tubing, the bottom plate and steel t-bolt hose clamps which were used to induce a compression seal between the O-ring and the tubing. Figures 1-4 show the components of the microcosm and its assembly.

***Microcosm Filling***

Homogenized sediment was transferred to microcosms and consolidated. To minimize soil disturbances, the Rhizon filters were pre-installed into tapped holes made in the microcosms. Pre-installing the filters allowed the microcosms to be thoroughly tested for leaks so as to prevent advection of fluid through the duration of the testing and allow for uniform consolidation of the sediment surrounding them. A plastic trowel was used to quickly transfer the sediment from the large mixing container to the microcosm to reduce exposure to the air. The sediment was consolidated using a concrete consolidation table with a variable frequency rheostat. For each site, an extra microcosm was prepared identically in order to measure solids density after an initial settling period by extracting a sub-core. Solids density in this extra microcosm will be used to provide a comparison of the test conditions with those measured in-situ.

***Overlying Water Mixing/Aeration***

A slow stream of air bubbles were introduced into the overlaying water through ¼ " PTFE tubing at approximately 10-25 % of the water depth (from the sediment) to provide a well-mixed, oxygenated system, similar to what would be experienced in-situ. Aquarium pumps (70 liters/min at 13.8 kPa) were used to push air through two filters and a saturation chamber. A HEPA filter in series with an activated carbon filter was used to ensure contaminants were not introduced into the microcosms through the air stream. The air was then pushed through a filter flask filled with site water in order to saturate the air with water vapor prior to bubbling through the microcosm overlying water and reduce evaporation within the microcosm. The air line runs out of the saturation flask, through a flow controller and into a polycarbonate gas manifold from which it was distributed to six microcosms through 1/8" ID Tygon lab tubing and PTFE tubing into the microcosm overlying water.

***Initial Characterization***

Subsamples of sediment for the characterization of initial conditions will be collected after the first (initial equilibration) phase of the experiment from sacrificial microcosms using 1-2 ” diameter polycarbonate tubes. Sacrificial microcosms were treated identically to experimental microcosms during Phase I but not sampled for pore water chemicals. Sediment samples will be sectioned analyzed for the same parameters as previously collected field cores (SO4, pH, iron, sulfide, DOC, AVS).

***Microcosm Experiment Design***

Experimental treatments: The experimental treatments will consist of incubating replicate (3) microcosms from each site at 21 degrees C and 4 degrees C with overlying water amended with sulfate and a tracer. An overlying water depth of ~10 cm will be carefully monitored and recorded in order to facilitate accurate flux measurements. An initial 1-month laboratory equilibration phase will take place with site water maintained at in-situ sulfate concentrations and chloride as a tracer. The second phase will be a 2-month sulfate dosing phase with overlying water amended and maintained with 300 mg/L sulfate plus bromide as a tracer. The third experimental phase will involve a 2-month return and maintenance of in-situ sulfate concentrations in the overlying water and fluoride as a tracer. Figure 5 includes a schematic of the experimental phases and timeline for measuring flux with overlying water measurements.

Overlying water composition: Overlying water amendments consist of a mixture of magnesium sulfate, sodium sulfate, and calcium sulfate designed to mimic water composition of mining-impacted streams on the Mesabi Iron Range. Tracers in the form of sodium chloride, sodium bromide, or sodium fluoride will be added for each respective phase of the experiment. Sulfate and chloride, bromide, and fluoride in site water immediately after collection was used to define in-situ sulfate concentrations and tracer levels for each phase of the experiment sufficiently large to be clearly identified above background in pore water samples. During each experimental phase, concentrations of sulfate and tracers in the overlying water will be monitored and may be amended with appropriate volumes of magnesium sulfate and sodium- tracer stock solutions when concentrations drop below 80-90% of their target values. Additional water will be collected from the site when necessary to periodically replace overlying water (minimum of once per experimental phase).

## Section B.2: Sampling Methods

***Overlying Water Collection***

Method: Samples from the overlying water will be collected from the PTFE tube used to bubble air into the overlying water into polypropylene syringes and filtered for analysis of anions (sulfate, chloride, bromide, fluoride) via Ion Chromatography. Sulfate and tracer concentrations will be carefully monitored in the well-mixed overlying water during each experimental phase in order to quantify the flux of chemicals into the sediment. The way in which a sample is processed, preserved, stored, and transported is determined by the laboratory and specific analytical procedure to be done on the sample. See Table 1 for what analyses are to be done on overlying water samples, the laboratory to do the analyses, and location in the Appendix of the analysis specific sampling requirements as defined in the laboratory's SOP.

Timing: Replicate samples (~5mL) will be collected from each microcosm and filtered approximately weekly during each experimental phase. It is expected that two-three sulfate flux estimates based on concentrations in the overlying water will possible during each experimental phase in order to quantify the transient changes in response to the treatment.

***Porewater Collection***

Method: Porewater samples will be collected with 5cm long Rhizon filters (0.2 µm) and 3 mL syringes. The Rhizon filters were installed prior to the microcosms being filled with sediment. Six filters were installed in a helix pattern around the perimeter of the tubing. The goal of this arrangement was to reduce the influence of sampling on the surrounding filters. Figures 3 and 4 illustrate the arrangement of the pre-installed filters. Filter assemblies consisted of a modified Rhizon filter sealed in a 1/8 " ID barbed to NPT fitting which was inserted into tapped holes in the microcosm body. The Rhizon sample line was sealed to the fitting using epoxy to seal a 1/8 "ID Tygon tubing sheath around both Rhizon sample line and NPT fitting. See Table 2 for what analyses are to be done on sediment porewater, the laboratory to do the analyses, and location in the Appendix of the analysis specific sampling requirements as defined in the laboratory's SOP.

Timing: It is expected that porewater samples will be extracted 2 times during each experimental phase, 2-5 days after the initiation of the phase and near the end of the experimental phase. Less than 4mL of water will be extracted in order to minimize the disturbance of the porewater profiles. The limited pore water volume will be prioritized for analysis of sulfate and other anions (Ion Chromatography), pH, sulfide, and ferrous iron.

***Final Sediment Collection and Characterization***

Method: In each microcosm, one 2 ½" diameter sediment core will be taken to identify and enumerate the various types of benthic microorganisms that may contribute to variations in flux of target analytes into and out of the sediment. Organisms will be filtered out of sediment samples using 500 micron sieves. Organisms are then immediately preserved in a solution of 70% alcohol (90% ethanol, 5% propanol, 5% methanol) and stored at 4° C in glass or plastic bottles

that are labeled by treatment and replicate number to be analyzed by MPCA aquatic organism experts for identification and quantification. The volume of sediment in each 2 ½" diameter core will be recorded to calculate concentration of organisms per given volume of sediment.

In addition, three or four 1" diameter sediment cores will be taken and composited per treatment replicate for analysis of total sulfur, AVS, total carbon and nitrogen, and % solids. Samples will be preserved based on the QA/QC requirements of the lab contracted to conduct the analyses. This information can be found in Table 3 of this document

Timing: The final microcosm coring for sediment collection and characterization will take place during the 2 to 3 days of the deconstruction phase of the experiment.

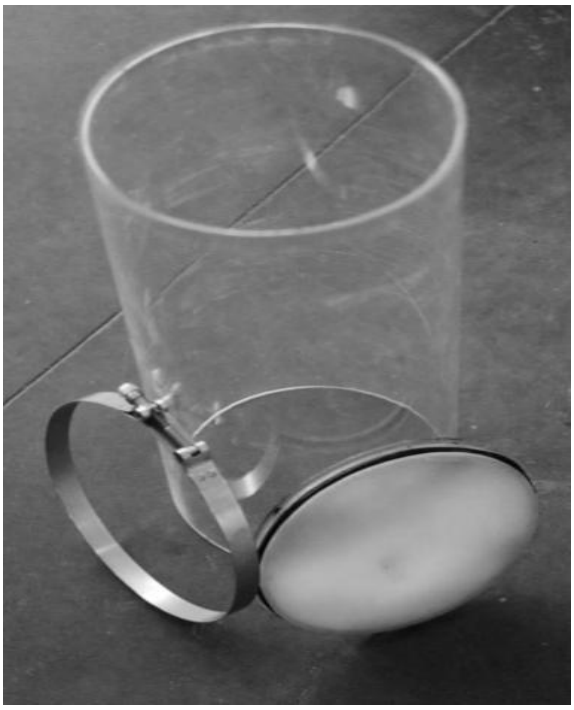


Figure 1: Acrylic Tubing, Polyester base and steel hose clamp

Figure 2: Assembled microcosm base

Figure 3: Side view of microcosm

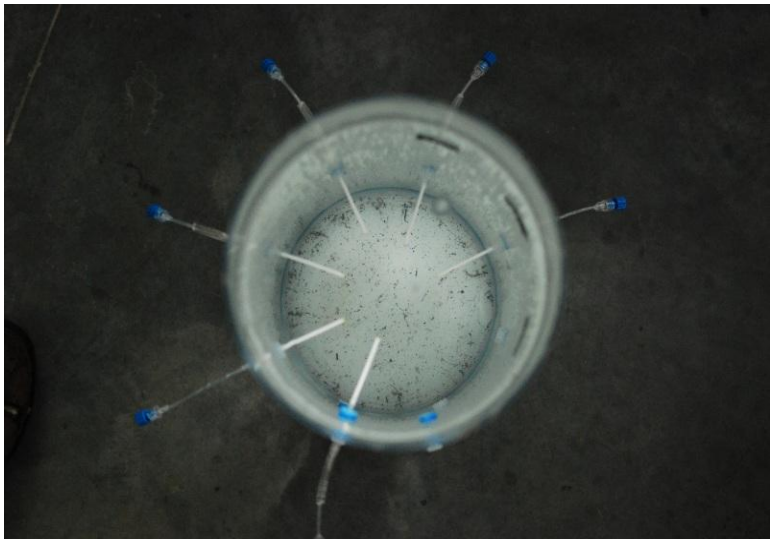


Figure 4: Top view of microcosm

## Section B.3: Sample Custody

### Section B.3.1: Overview

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

### Section B.3.2: Microcosm Sampling Custody Procedures

The microcosm sampling personnel either have the samples in their possession, in their view, in a secured area that only they have access to, or turn custody over to another individual who has signed the chain of custody (COC) form (See Attachment 3 for an example COC form). The COC is the record of all individuals who come in contact with the samples. A copy of the chain of custody is maintained at all times to ensure the samples can be used in for enforcement. A COC has the following information present:

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

Sample custody is maintained from collection through analysis. The samples are cooled on ice. The chain of custody form is signed by the sampler and double zip-locked and taped to the inside lid of the cooler. The cooler is custody taped on two corners and shipped if laboratory analyses are to be performed at the MDH. The sampler and the laboratory keep a copy of the bill of lading as proof of custody in shipment. Records of custody are maintained by the MPCA within the site files.

### Section B.3.3: Laboratory Custody

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

The laboratory stores the samples in a secure refrigerated area that maintains the samples at 4° +/- 2° C. The sample holding area is secure from unauthorized personal having access to the samples. The samples are removed by an analyst for extraction/digestion, the extraction/digestion performed, and any remaining sample placed back in the refrigerator. The

laboratory disposes of the samples, except in case of very hazardous samples, which are then returned to the site or lab-packed for disposal at an appropriate facility.

## Section B.4: Analytical Methods

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

## Section B.5: Quality Control

Laboratory QC checks are identified in Table 2. The frequency of analysis and the control limits are also listed. If the results don't meet the QC acceptance criteria, corrective actions are defined.

### Section B.5.1: QC Types

#### Table 4: Quality Control Elements

| QC Type | Surface Water | Porewater | Sediment |
|---|---|---|---|
| Blanks | | | |
| Method Blanks | 1 per batch | 1 per batch | 1 per batch |
| Spikes | | | |
| Laboratory Control Sample (LCS) | 1 per batch | 1 per batch | 1 per batch |
| Matrix Spike (MS) | 1 per batch | 1 per batch | 1 per batch |
| Calibration Checks | 1 per batch | 1 per batch | 1 per batch |
| Duplicates | | | |
| Laboratory Duplicates | 1 per batch | 1 per batch | 1 per batch |
| Matrix Spike Duplicate (MSD)(if conducted) | 1 per batch | 1 per batch | 1 per batch |
| Laboratory Control Sample Duplicate (LCSD) (if conducted) | 1 per batch | 1 per batch | 1 per batch |

#### Table 5: QC Acceptance Criteria for Target Analytes in Surface Water and Porewater

| Target Analyte | Blanks | LCS (%R) | MS (%R) | Laboratory Duplicates (RPD) | Laboratory | Appendix |
|---|---|---|---|---|---|---|
| Dissolved Oxygen | N/A | N/A | N/A | N/A | UMD Civil Engineering | Appendix D |
| Conductivity | N/A | N/A | N/A | N/A | UMD Civil Engineering | Appendix D |
| pH | N/A | N/A | N/A | N/A | UMD Civil Engineering | Appendix D |
| Temperature | N/A | N/A | N/A | N/A | UMD Civil Engineering | Appendix D |
| Ferrous Iron | <RL | 85 – 115 | 85 – 115 | 25 | UMD Civil Engineering | Appendix D |
| Sulfate | <RL | 90 – 110 | 90 – 110 | 25 | UMD Civil Engineering | Appendix D |
| Chloride | <RL | 90 – 110 | 90 – 110 | 25 | UMD Civil Engineering | Appendix D |
| Bromide | <RL | 85 – 115 | 85 – 115 | 25 | UMD Civil Engineering | Appendix D |
| Fluoride | <RL | 85 – 115 | 85 – 115 | 25 | UMD Civil Engineering | Appendix D |
| Sulfide | <RL | 85 – 115 | 85 – 115 | 25 | UMD Civil Engineering | Appendix D |
| Sulfide | <RL | 85 - 115 | 85 – 115 | 25 | UMD Civil Engineering | Appendix D |
| Phosphate | <RL | 85 – 115 | 85 – 115 | 25 | MDH | Appendix C |
| Nitrogen | <RL | 85 – 115 | 85 – 115 | 25 | MDH | Appendix C |

**Table 6: QC Acceptance Criteria for Target Analytes in Sediment**

| Target Analyte | Blanks | LCS (%R) | MS (%R) | Duplicates (RPD) | Laboratory | Appendix |
|---|---|---|---|---|---|---|
| Acid Volatile Sulfide (AVS) | <RL | 70-130 | 80-120 | 50 | MDH Environmental | Appendix C |
| ICP-MS for Extractable Metals | <RL | 70-130 | 80-120 | 50 | UMD CE | Appendix D |
| Total Sulfur | <RL | 70-130 | 80-120 | 50 | LacCore/LRC | Appendix E |
| Total Carbon | <RL | 70-130 | 80-120 | 50 | LacCore/LRC | Appendix E |
| Total Nitrogen | <RL | 70-130 | 80-120 | 50 | LacCore/LRC | Appendix E |
| Percent Solids | <RL | 70-130 | 80-120 | 50 | MDH Environmental | Appendix C |

### *Section B.5.1.1: Method Blanks*

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

### *Section B.5.1.2: Matrix Spikes (MSs)*

Matrix spikes may be used by a laboratory to determine if there are any effects related to the sample matrix. One spike should be spiked, prepared, and analyzed per batch of up to 20 samples. The % recoveries of the MS are used to measure accuracy of the analysis. The % recoveries should be within the ranges listed in Tables 4, 5, or 6. Refer to the laboratory's QAM (if available) or specific analytical method located in the appendix of this QAPP for details of this QC activity.

### *Section B.5.1.3: Laboratory Control Sample (LCS)*

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 % recoveries of the LCS are used to show that the analysis is in control if there is a matrix effect associated with the analysis of the sample matrix in the MS. The % recoveries should be within the ranges listed in Tables 5 and 6. Refer to

the laboratory's QAM (if available) or specific analytical method located in the appendix of this QAPP for details of this QC activity.

#### *Section B.5.1.4: Laboratory Duplicates*

Laboratory duplicates are used to measure precision. One pair should be extracted and analyzed per ten samples or less. The RPD should be less than or equal to the values listed in Tables 4, 5, and 6.

#### *Section B.5.1.5: Out-of-Control Situations*

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

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

### Section B.6.1: Laboratory Equipment

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

## Section B.7: Instrument/Equipment Calibration and Frequency

### Section B.7.1: Overview

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

### Section B.7.2 Laboratory Procedures

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

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

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

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

## Section B.9: Data Management

Internally, each agency will store all data in their own specific StarLIMS database (Laboratory Information Management system). Data will be transferred from the laboratories to the MPCA. Data will be stored in a Microsoft Access database at MPCA for data processing and analysis.

### Section B.9.1: Data Recording

Data and information collected in the lab will be recorded in dedicated notebooks and forms. Data recording procedures to be followed by the laboratory are discussed in individual laboratory's QAM, if available.

### Section B.9.2: Data transformation

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

### Section B.9.3: Data Transmittal

Data and laboratory 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 MPCA and summaries of the project activities will be presented at the February 2013 Conference.

### Section B.9.4: Data Rejection

Analytical data which does not meet the established QA/QC criteria defined in this QAPP is verified and either flagged as estimated or rejected.

### Section B.9.5: Data Tracking

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

### Section B.9.6: Data Storage and Retention

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

# Section C: Assessment and Oversight

## Section C.1: Response Actions

### Section C.1.1: Laboratory Audits

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

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

### Section C.1.2: Performance Evaluation (PE) Studies

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

## Section C.2: Corrective Action/Reports to Management

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

### Section C.2.1: MPCA Corrective Actions

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

### Section C.2.2: Laboratory Corrective Actions

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

### Section C.2.3: Laboratory Reports

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

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

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

### Section C.2.4: Reports to Management

Reports to management will summarize the Project's sampling and analytical activities for the previous time period, the findings of the audits, any required corrective actions, the results of PE studies, any data quality problems (along with purposed solutions), any major changes in personnel, and an overall evaluation of the laboratory's quality assurance. The report is sent to all individuals identified in Section A.4.

# Section D: Data Validation and Usability

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

### Section D.1.1: Data Reduction

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

### Section D.1.2: Data Verification/Methods

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

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

### Section D.1.3: Data Validation/Methods

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

## Section D.2: Reconciliation with User Requirements

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

## Section D.3: References

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

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

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

## Appendix A: Table of Acronyms

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

# Appendix B: MDH Environmental Laboratory QA Manuals

# Quality Assurance Manual

for the

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

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

**CONTROLLED DISTRIBUTION**

**COPY #:** **1 of 1**

**ISSUED TO:** **PHLD Intranet**

**Quality Assurance Manual, Revision 9**

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

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

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

Table of Contents

# Appendices

## Table of Contents

## SECTION 1.0: LIST OF ACRONYMS

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

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

## SECTION 2.0: DEFINITIONS OF QC TERMS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**Duplicate:** See field duplicates or laboratory duplicates.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where:

S = Standard Deviation
X = Mean value

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**Reagent Blank (RB):** See Method Blank.

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

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

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

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

where:

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

OR more simply:

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

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

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

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

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

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

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

**Run:** See analytical run.

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

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

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

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

**Should:** Denotes a recommended but not required action.

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

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

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

**Standard Curve:** See calibration curve.

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

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

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

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

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

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

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

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

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

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

## SECTION 3.0: GENERAL LABORATORY INFORMATION AND POLICIES

### A. Organization

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

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

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

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

B. Facility Description and Location

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

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

C. Building Security

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

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

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

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

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

**SECTION 4.0:** POLICIES

A. Quality Assurance Policy

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

B. Ethics Policy

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

C. Data Practices Policies

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

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

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

**SECTION 5.0:** PERSONNEL

A. Positions and Responsibilities

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

Environmental Laboratory Management Team: authorizes training and development for

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

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

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

B. Training

1) General Employee Training (for all staff)

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

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

Quality Assurance Manual Agreement

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

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

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

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

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

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

2) Radiation Safety Training (for selected staff)

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

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

3) Initial Demonstration of Capability (for laboratory analysts)

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

4) Ongoing Demonstration of Capability (for laboratory analysts)

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

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

## SECTION 6.0: INFORMATION TECHNOLOGY

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

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

system.

B. Computer Security

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

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

C. Additional Software

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

## SECTION 7.0: SAMPLING

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

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

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

## SECTION 8.0: SAMPLE CUSTODY, HANDLING AND TRACKING

A. Receiving Hours

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

B. Sample Acceptance/Rejection Criteria

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

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

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

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

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

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

C. Civil or Criminal Chain-of-Custody Procedures

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

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

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

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

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

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

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

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

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

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

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

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

times.

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

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

D. Data Records for Custody Samples

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

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

E. Sample Custodians

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

F. Additional Instruction

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

G. Sample Tracking

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

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

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

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

H. Subcontracting of Analytical Services

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

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

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

I. Sample Storage

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

J. Sample Disposal

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

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

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

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

K. Records Retention

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

## SECTION 9.0: DATA QUALITY OBJECTIVES

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

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

## SECTION 10.0: ANALYTICAL PROCEDURES

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

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

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

## SECTION 11.0: EQUIPMENT AND SUPPLIES

A. Maintenance

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

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

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

B. Monitoring Conditions

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

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

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

C. Procurement of Supplies

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

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

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

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

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

## SECTION 12.0: CALIBRATION

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

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

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

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

## SECTION 13.0: QUALITY CONTROL

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

B. Detection Level

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

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

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

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

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

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

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

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

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

A. Reduction and Validation Process

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

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

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

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

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

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

B. Reporting

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

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

## SECTION 15.0: SYSTEM AUDITS

A. Proficiency Testing

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

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

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

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

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

B. Internal Audits

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

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

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

C. External Audits

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

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

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

D. Corrective Action Policy

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

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

## SECTION 16.0: REFERENCES

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

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

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

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

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

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

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

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

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

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

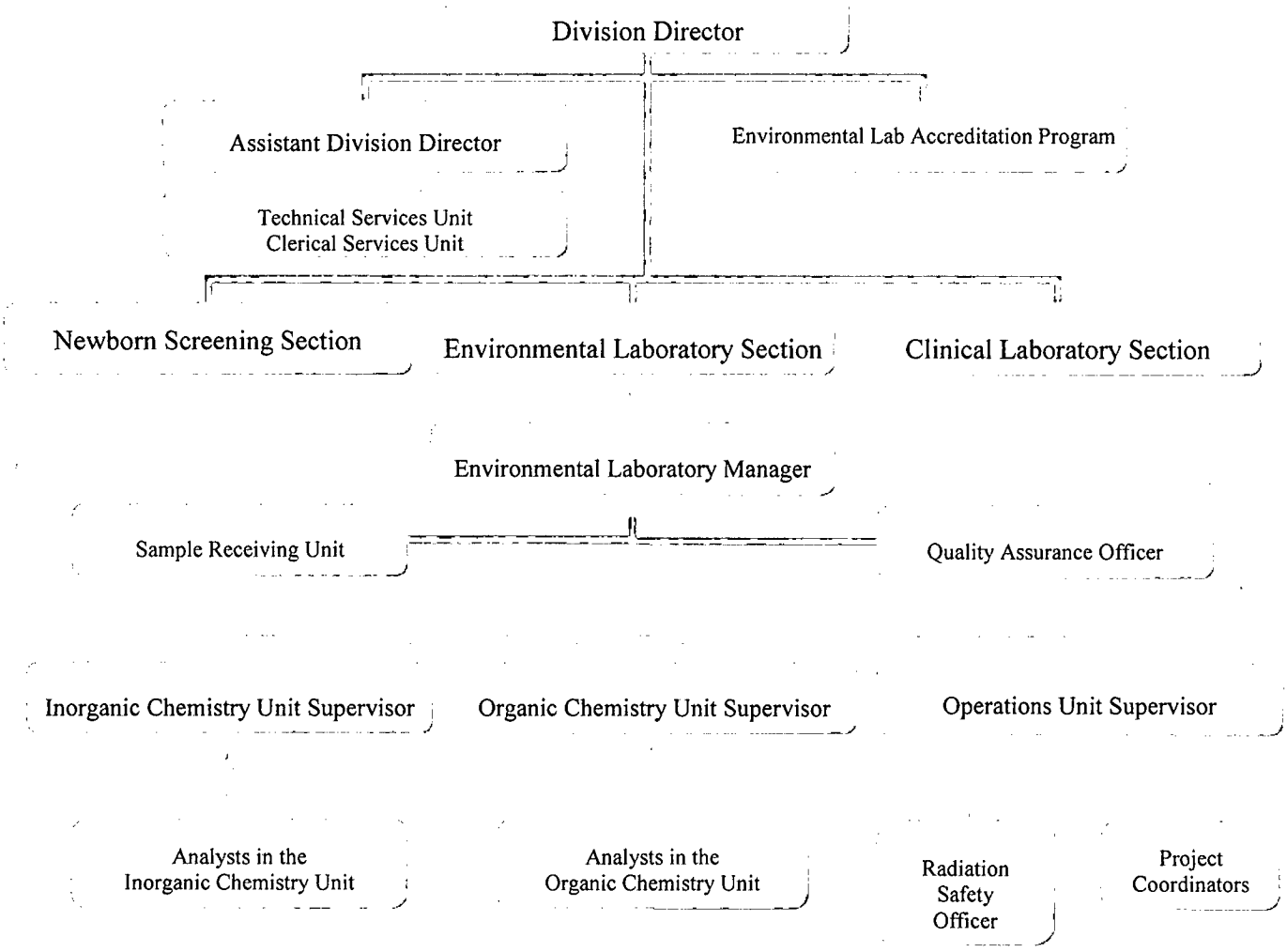
Minnesota Department of Health Environmental Laboratory Sample Receiving Procedure Manual, Rev. 4, Laboratory Information Management Systems and Technical Services Section (2006).

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

## SECTION 17.0: APPENDICES

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

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



# Appendix 2
# Training Record for an Individual Standard Operating Procedure

MDH Environmental Laboratory

Document Number: 2006-02

ANALYST: _____ ANALYSIS / AN CODE: _____

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

Additional Comments and Notes:

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

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

_____
trainer 1 signature / date

_____
trainer 2 signature / date

_____
analyst signature (at completion of training) / date

# Appendix 3
# Record of Personnel Education and Training

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

Document Number : 2006-01 .

**Record of Personnel Education and Training**

Please Print

**Employee Name:** _____
**Job Title:** _____

Instructions are on the back of this sheet.

| Date | Type of Instruction | Training Activity | Trainer's Name | Hours |
|---|---|---|---|---|
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

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

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

| 1 | 2 | 3 | 4 |
|---|---|---|---|

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

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

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

Lab Comments

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

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

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

Rev. 11/07/2008

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

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

| A | B | C | D | E |
|---|---|---|---|---|
| | | | | |

Minnesota Pollution Control Agency

**MDH Stream / Lake Lab Sheet**

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

MDH ID:_____ Report to: _____ Phone: _____

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

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

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

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

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

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

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

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

MINNESOTA MDH DEPARTMENT OF HEALTH

**Chain of Custody**

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

Page ____ of ____

Lab Use Only.

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

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

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

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

Report to_____
MDH ID_____
_____
_____
_____
Address If Needed

Sampled By (Print) Affiliation
Sampler Signature Phone

Containers & Preservatives

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

Sampler Comments:

Receiving Comments:

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

White Client Copy  Yellow Lab Copy  Pink Submitter Copy

MDH 1000

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

000250

MDH-CHEMICAL LABORATORIES
CHAIN OF CUSTODY LOG

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

CUSTODY TRANSFER RECORD

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

COMMENTS_____

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

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

**Perkin-Elmer Elan DRC II Daily Maintenance**

Serial Number: Z0130310 Month: May Year: 2009

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

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

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

**Perkin-Elmer Elan DRC II Monthly Repairing and Maintenance Log**

Serial Number: **Z0130310** page 1

| DATE | WHO | PROBLEM & SOLUTIONS |
|---|---|---|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

# Appendix 8

## Policy and Procedure for Detection Level Study

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

MDL = Std.Dev. x Student's t

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

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

MDL = _____

TV/MDL = _____

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

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

QAO Comments:

Approved by QAO: _____
Init. & date

MDL Study entered: _____
Init. & date

## MDL Single Analyte Worksheet Instructions

*prepared by Keith Peacock, 2-23-07*

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

16. Then answer the questions shown.

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

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

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

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

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

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

## Formulas for the MDL Single Analyte Worksheet

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

*prepared by Jesse Fillmore, March 2007*

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

# Appendix 10

## Policy and Procedure for Initial Demonstration of Capability Study

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

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

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

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

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

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

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

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

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

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

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

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

# Appendix 11

## Policy and Procedure for Report Level Verification

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

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

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

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

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

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

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

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

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

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

# Appendix 12
# USEPA Certification for Laboratory Analyses for Drinking Water

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

AUG 29 2008

REPLY TO THE ATTENTION OF

WG-15J

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

Dear Dr. Liao:

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

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

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

Sincerely,

Thomas Poy

for Timothy C. Henry
Acting Director, Water Division

Enclosure

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

# USEPA Certification for Laboratory Analyses for Drinking Water

ENCLOSURE A

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

| Parameters/Method | Certification Status |
|---|---|
| 1. Metals-ICP-AES/ 200.7<br>* Barium<br>* Calcium<br>* Copper<br>* Iron<br>* Magnesium<br>* Sodium | Fully Certified |
| 2. Metals-ICP-MS / 200.8<br>* Aluminum<br>* Antimony<br>* Arsenic<br>* Barium<br>* Beryllium<br>* Cadmium<br>* Chromium<br>* Copper<br>* Lead<br>* Manganese<br>* Nickel<br>* Selenium<br>* Silver<br>* Thallium<br>* 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<br>* Bromate<br>* Chlorite<br>* Bromide<br>* Sulfate<br>* Chloride | Fully Certified |
| 12. Total Organic Carbon / SM5310 C | Fully Certified |
| 13. Carbamates / 531.1<br>* Aldicarb<br>* Aldicarb Sulfone<br>* Aldicarb Sulfoxide<br>* Carbaryl<br>* Carbofuran<br>* 3-Hydroxycarbofuran<br>* Methomyl<br>* Oxamyl | Fully Certified |
| 14. EDB and DBCP/504.1<br>* 1,2-Dibromoethane<br>* 1,2-Dibromo-3-chloropropane | Fully Certified |

# USEPA Certification for Laboratory Analyses for Drinking Water



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

# USEPA Certification for Laboratory Analyses for Drinking Water



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

# Appendix 13
# Corrective Action Form for Non-conforming Work




## Corrective Action Form (CAF)

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

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

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

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

Analyst/Investigator: _____ Report Value: _____

Sample Number(s): _____ True Value: _____

Analysis Date: _____ Control Limit Ranges: _____

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

**Description of Problem:** *check those that apply*

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

___ The unapproved use or modification of an Standard Operating Procedure

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

___ Internal or external audit deficiencies

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

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

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

___ Other, please explain:

_____

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

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




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

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

**Operations/Data Affected:**

**Corrective Action Taken:**

**Results of Corrective Action/Data Corrected:**

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

_____ Analyst/Initiator (signature & date)

_____ Unit Supervisor (signature & date)

_____ Quality Assurance Officer (signature & date)

_____ Laboratory Section Manager (signature & date)

*Original: Quality Assurance Officer*

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

# Minnesota Department of Health
# Environmental Laboratory

## Sample Acceptance Policy

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

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

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

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

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

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

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

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



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

MINNESOTA MDH DEPARTMENT OF HEALTH

# Sample Receiving Procedure Manual

For the

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



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

Approvals:

Andrew Mittendorff
Lead Worker, Sample Receiving

Laura Fischer
Supervisor, Laboratory Services

Gary Jones
Information Systems Manager

Stephanie Drier
QA Officer, Environmental Laboratory

# TABLE OF CONTENTS

# INTRODUCTION TO SAMPLE RECEIVING

## CLIENTELE

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

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

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

**Federal Clients:**

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

**Private Companies:**

1. Northshore Mining
2. LTV Steel

## PROGRAM CODES

### Program/Client Specific Codes

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

### Miscellaneous Program Code

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

### Laboratory Consult/Non-Billable Program Code

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

### Quality Control Code

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

### Environmental Health Codes

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

### Department of Transportation Codes

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

### Pollution Control Agency Codes

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

## DATA SHEETS

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

## GENERAL TASKS

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

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

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

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

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

# COMPUTER OPERATIONS

## OVERVIEW OF SAMPLE ENTRY SCREENS

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

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

### Editing

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

### Entry

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

### Logs/Lists

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

### View

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

## INITIAL DATA ENTRY PROCEDURE

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## REJECTION PENDING LIST PROCEDURE

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

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

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

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

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

## EDITING SAMPLE ENTRY INFORMATION

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

**Using the Editing: Init Entry Screen**

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

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

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

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

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

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

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

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

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

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

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

**Editing Field and Trip Blank information**

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

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

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

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

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

5. Repeat as needed to edit additional samples.

## USING THE VIEW SCREENS TO FIND SAMPLE RECORDS

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

### Lab Review Screen

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

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

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

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

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

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

### PWS Table Review

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

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

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

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

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

## USING LAB REVIEW TO FIND A PROGRAM CODE

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

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

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

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

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

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

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

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

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

## ADMINISTRATIVE CODES

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

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

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

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

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

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

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

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

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

## NUMBERING ERROR CORRECTION PROCEDURES

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

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

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

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

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

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

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

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

# CHAIN-OF-CUSTODY

## CUSTODY FORMS

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

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

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

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

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

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

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

## C-of-C SAMPLE PROCESSING PROCEDURE

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

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

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

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

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

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

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

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

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

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

10. Attach the labels to the samples.

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

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

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

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

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

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

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

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

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

# PRIORITY LEVELS

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

There are four priority levels.

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

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

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

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

## PRIORITY SAMPLE PROCEDURE

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

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

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

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

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

5. Attach the labels to the samples.

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

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

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

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

**Maximum Analytical Times/Priority Options Chart**

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

# SPECIAL SAMPLE HANDLING

## ORGANICS SAMPLES

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

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

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

## BACTI/CHEM SAMPLES

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

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

## OSHA SAMPLES

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

## MICROPARTICULATE SAMPLES

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

# SAMPLE RECEIVING EQUIPMENT

## LABEL PRINTER

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

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

**Installing labels in the printer**:

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

**Installing a new ribbon**:

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

## DATE/TIME CLOCK

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

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

## PHOTOCOPIER

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

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

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

## FAX MACHINE

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

# SAMPLE RECEIVING MONTHLY REPORTS

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

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

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

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

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

## CREATING THE MONTHLY REPORT

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

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

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

# HOLD TIMES LIST

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

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

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

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

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

## TESTS WITH A 2 DAY (48 HOUR) HOLD TIME

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

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

## TESTS WITH A 3 DAY HOLD TIME

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

## TESTS WITH A 4 DAY HOLD TIME

809 Radon

## TESTS WITH A 5 DAY HOLD TIME

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

## TESTS WITH A 7 DAY HOLD TIME

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

## TESTS WITH A 14 DAY (2 WEEK) HOLD TIME

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

## TESTS WITH A 28 DAY (4 WEEK) HOLD TIME

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

## TESTS WITH A 30 DAY HOLD TIME

450 Chlorophyll A, field filtered
451 Pheophytin A

## TESTS WITH A 6 MONTH HOLD TIME

Preserved metals (except mercury)

# ENVIRONMENTAL HEALTH SAMPLES

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

**Division: Environmental Health**

*Section: Drinking Water Protection*

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

2. Non-Community Public Water Supply

3. Source Water Protection*

**EH-PWS IDENTIFICATION NUMBERS AND PROGRAM CODES:**

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

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

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

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

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

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

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

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

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

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

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

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

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

# ENVIRONMENTAL HEALTH DATA SHEETS

## MDH DATA SHEET

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## EH SAMPLES FROM NON-MDH COLLECTORS

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

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

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

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

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

# SAMPLE PROCESSING PROCEDURE

## SAMPLE DELIVERY SCHEDULE

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

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

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

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

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

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

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

## CHECKING BOTTLES FOR IDENTIFICATION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

## NUMBERING THE SAMPLE DATA SHEETS

Use the Rapidprint Machine to number the samples.

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

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

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

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

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

## SAMPLES SUBMITTED WITHOUT A LAB SHEET

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

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

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

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

## LABELING THE SAMPLE CONTAINERS

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

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

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

The labels will print out grouped by bottle type. The upper right label for each group should describe which bottle they are for.

**Special Sample Bottle Labeling**

***BOD/CBOD samples***: As part of the processing of these samples the lab will submerge them in water, so the regular labels will not work. Using a black sharpie permanent marker, write the sample number on a 1 x 2-1/2" white shamrock label. Place this label on the shoulder of the bottle and deliver the printed labels along with the samples to the lab.

***Chlorophyll/Pheophytin filter***: Unwrap the filter(s) and make sure the filtered volume is written on the petri dish. If it is not, check the data sheet for this info and write it on the dish. If the volume is not on the data sheet either, call the collector. Place one label with just the sample number (no test code) on the petri dish containing the filter. Do not cover any information written on the dish. Re-wrap the filter or group of filters in foil. Place another label with sample number only on the foil. For a group of samples, use a label from the first and last numbers only; it is not necessary to put a label from each number on the foil. Clip all of the labels from one group together and save them for delivery to the lab.

***Total/Ortho Phosphate samples***: These samples are collected by community systems on behalf of Environmental Health. They are collected in an unpreserved nutrient bottle. Put the Total Phosphorus label on the bottle as normal. For the Ortho label, peel back 1/3 of the backing and stick it to the cap.

***Multiple program samples***: Occasionally the MPCA will submit samples that they want analyzed under two different programs. The sheets are given separate numbers and the labels are attached similarly to phosphate samples. One programs label on the side of the bottles and one on the top.

***Metals bottles***: Place the entire label on the bottle. Peel off one label with just the sample number and place on top of the bottle cap. The metals lab holds samples for several months.

Having the numbers visible from the top makes it easier for them to find samples on their carts

***Organics bottles***: Place one small label with the sample number and test code on the upper part of the bottle or vial. Most organic analyses will have their own bottle so the lab doesn't need the rest of the labels.

***Radiation samples***: Place one small label with just the sample number on the samples and save the rest of the label for delivery to the lab. For samples that have a paper tag, put the label on the tag.

***Duplicate sample containers***: Sometimes collectors will submit more than one of the same type of container for a sample. In these cases write "1 of 2" or "2 of 2" on a single label and put it on each container. Attach the rest of the labels to one of the containers or deliver them to the lab separately as needed.

***OSHA samples***: Do not remove the samples from their bags (the labs will do this). Just clip the labels and paperwork to the bag containing the samples. People in the labs will deal with labeling themselves.

## PRINTING SAMPLE ENTRY LOG AND COMPARING TO DATA SHEETS

After samples have been delivered to the lab print a Daily Entry Log and compare it to the data sheets.

1. From the main screen select **Log/lists** and pull-down to select **Daily Entry log**.

2. Type in the beginning and ending sample numbers for the lab sheets.

3. Select the printer "Labserv 2" to print the log list.

4. The log will list all the sample numbers with some basic information about each one. The information we are checking for is: ***Program Code, Analysis Codes, Priority,*** and ***Field/Trip Blank***. As you are checking the samples, draw a line along the log list to indicate to Clerical staff that the log has been verified.

5. If there are any errors make changes using the edit screens and note the changes on the log list. If any analysis codes were entered incorrectly it is necessary to reprint the corrected labels. Find the sample bottles in the lab and attach the correct labels.

6. When you are finished paper clip the log list on top of the stack of lab sheets and deliver it to clerical. There is a basket for incoming work in the filing room.

# DELIVERING SAMPLES TO THE LABORATORY

Deliver samples with short hold times first and notify lab personnel. It may be helpful to load samples onto the transport cart in the same order that they will be needed in the labs. Refer to the following descriptions for the correct ordering method.
Refer to the **Labs Map, South** for the following sample delivery locations.

**C-of-C Room**: All Chain of Custody Samples must go in the locked cooler in this room. The C-of-C log book is also located here.

1. Place ***radon*** samples in racks on this counter.

2. Place all other ***radiation chemistry*** samples on this lab counter and put extra labels in the basket. If it is late in the day and no one is in the radiation area put milk, crops, or other perishable samples into the fridge (**2a**).

3. Place all ***metals*** samples on this counter. Put samples in order left to right and front to back. Line up Metals samples and Mercury samples separately. Put any non water samples just to the right.

4. This is the preserved samples bench. There are trays for three different sample bottles; ***cyanide, nutrient*** and ***nitrate***. All bactichem samples should be lined up in order, left to right and back to front (except as noted). When a tray is full (or the tray is missing) more can be found in the cabinet just below the counter.

5. There are two trays on this counter. ***Nitrite*** samples go on the tray to the right, ***fluoride*** samples go on the tray to the left. The lab only runs fluorides every few weeks so the samples tend to accumulate. When a tray is full put a new tray on top and continue to line up samples as before.

6. This is the ***general*** (unpreserved) samples counter. There are not specific trays since many different types of samples and bottles are placed here. Try to keep similar samples grouped together as much as possible. In addition to samples collected in general bottles, any sample that is unpreserved should go on this counter. ***BOD/CBOD*** samples are placed on this counter, with the printed labels paper clipped together and sitting on top of the bottles for the lab analysts. The baskets for chlorophyll labels are located on this counter, just to the right of where the samples are put.

7. Put ***chlorophyll filters***, wrapped in tinfoil in this freezer; labels go in the (field-filtered chlorophyll) basket on the general counter (**6**).

8. Put chlorophyll bottles in the walk in cooler. Line them up on the shelves in the back left corner. Labels go in the (lab-filtered chlorophyll) basket on the general counter (**6**).

9. ***Cryptosporidium*** filters or water jugs go on the middle shelf just inside the cooler door.

10. ***Bromate/Chlorite*** samples should be collected in 250ml unpreserved plastic bottles, wrapped in tinfoil. Place them on the middle shelf in the cooler.

11. All ***bacteriological*** samples are placed on this counter. Line up samples in groups of five, front to back and right to left. For non routine bacti analyses, put copies of the lab sheets on top of the samples for the lab analysts.

12. Put copies of ***cryptosporidium*** lab sheets on this counter.

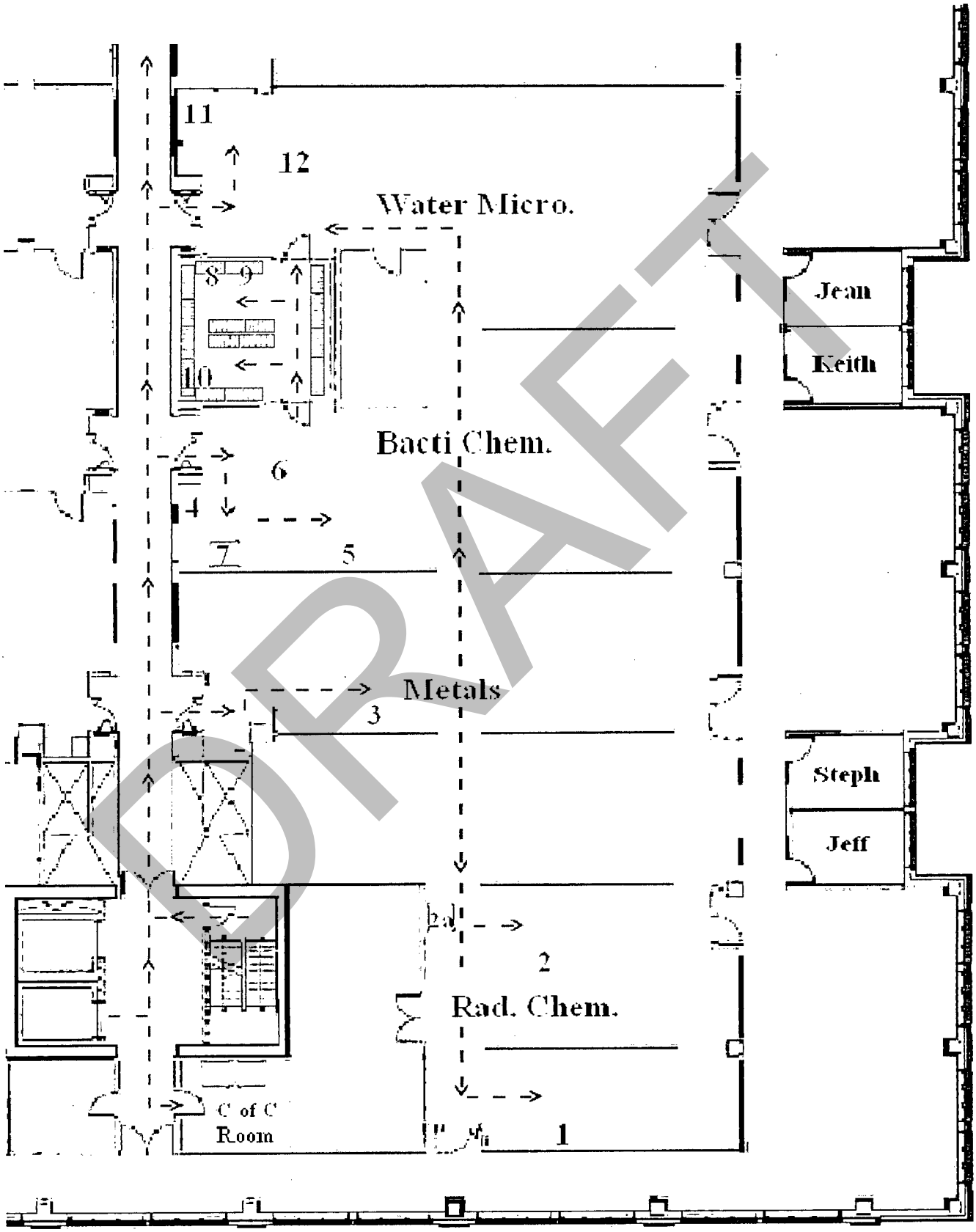
Refer to the **Labs Map, North** for the following sample delivery locations.

1. Most non-volatile organics samples, (***PFOS , SOC, PCB, SVOC, etc***) are placed in this refrigerator. This cooler is often quite full, but try to follow the shelf labels for the correct placement of samples. For PFOS samples, put a copy of the lab sheets on Julia's desk. For other non-routine samples, leave a copy of the lab sheet with the samples in the cooler.

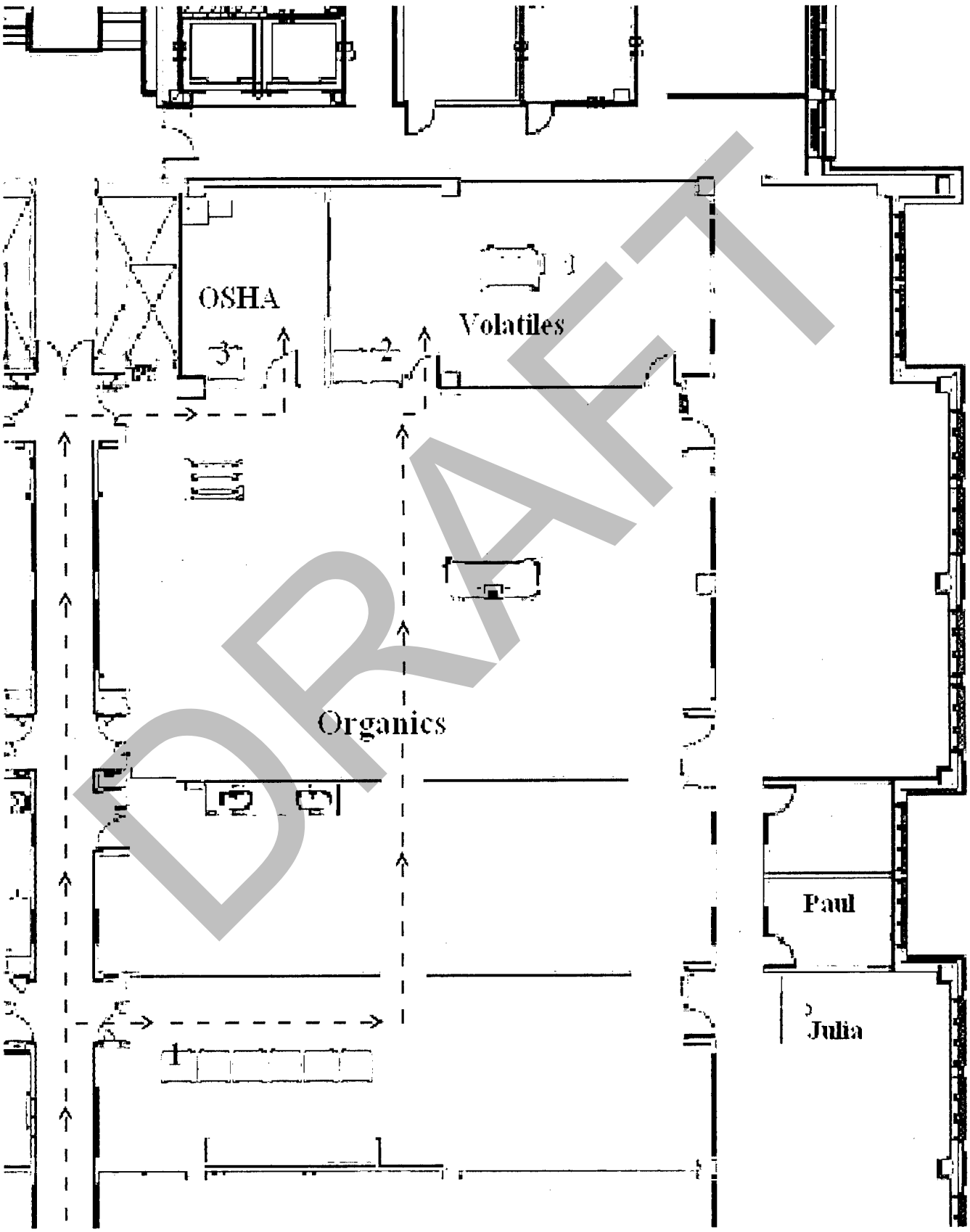
2. ***All volatile organics*** samples go in this fridge. The top two shelves are for 468 VOCs, the lower shelves are for 498 VOCs. Lab sheet copies go in the basket just opposite the cooler.

3. ***OSHA organics samples*** go in the locked half-size cooler in this room. Paperclip the bagged samples, labels and original lab sheets together and place in the cooler.

## LABS MAP, SOUTH


11
12
Water Micro.
8
9
10
Jean
Keith
Bacti Chem.
6
4
7
5
Metals
3
Steph
Jeff
2a
2
Rad. Chem.
C of C
Room
1

## LABS MAP, NORTH



# MINNESOTA POLLUTION CONTROL AGENCY (MPCA) SAMPLES

The MPCA collects a great variety of samples from numerous locations around the state. They submit water samples from lakes, streams, rivers, feedlot run-off, closed landfill monitoring wells, drinking water (rarely), Superfund sites, etc. They also submit sediment/soil, sludge, fish, filters, paint and other samples. They collect some samples on a routine basis for monitoring purposes. In other cases, they respond to complaints, spills, fish kills or other crises.

The MPCA submits most of the high priority and Chain-of-Custody samples that we receive. They also submit most of our sediment/soil, fish, sludge and paint samples.

Shipping Protocol:
Most MPCA samples are transported/shipped on ice, in coolers because they are supposed to be maintained at a temperature of 4 degrees Celsius or less. The temperature needs to be checked and noted when the samples arrive.

Program Codes:
The MPCA uses over 50 different MDH Program Codes. There are a few that are used for routine samples, but many that are specialized. It is nearly impossible for us to determine the correct code if it is not provided by the collector. The routine codes are as follows:

PC MPCA-23 EOD-Lake Monitoring
PG MPCA-27 EOD-Routines
QW MPCA Closed Landfill Assessment

## MPCA SAMPLE PROCESSING PROCEDURE

The MPCA courier delivers most of the samples we receive from them. Samples may be delivered by other courier services depending on where they are coming from.

Open coolers and boxes carefully. You may need to use a retractable blade "Exacto" knife to cut through the sealing tape. It is advisable to wear safety glasses while using a knife. Make sure that data sheets were included with the samples. Collectors usually put data sheets in plastic bags to protect them from moisture and they sometimes tape the bag to the lid of the cooler. If there are no data sheets (a very rare occurrence), refer to the return address to help you track down the collector. At the very least, you would then be able to contact the MPCA office that the samples were shipped from.

RECEIVING SAMPLES AND DATA SHEETS VIA IN-PERSON DELIVERY

When the MPCA courier (Ed Norwig) delivers samples, he will arrange them in order, on the counter. He never delivers samples without data sheets.

When other MPCA collectors bring in their samples, ask them to arrange them in order, on the counter. Make sure they filled out their data sheets completely and correctly. Do not allow

them to leave until the data sheet is complete and you have had a chance to compare the sample containers to the data sheets. In other words, go through steps 4,5,6,7, & 8 before the collector leaves.

CHECKING THE TEMPERATURE OF SAMPLES UPON ARRIVAL:

We normally check the sample temperature by using a temperature blank bottle that is kept in the cooler with the samples (see background information). It is most important to record the temperature information for bacteriology, BOD and Organic samples, but we should record it for all types of samples.

The MPCA courier takes and records the temperature for the samples he brings in and most other MPCA collectors do this for their own samples as well.

If there is no temperature blank, use a general bottle (be sure to clean the thermometer thoroughly first).
If there is no general bottle, you may use water that has pooled in the bottom of the cooler.
If there is no pooled water, but the samples are on ice or freezer packs, record the comment "no temperature blank, but samples on ice" on the data sheet.
If the samples are not on ice, record the comment "no temperature blank, samples not on ice".
If there is ice IN a sample, also make note of this.

CHECKING DATA SHEETS AND COMPARING THEM TO THE SAMPLE CONTAINERS:

Make sure there is a Program (Billing) Code on the Data Sheet. We cannot enter any information in the computer without a program code. If there is no code, contact the collector or the "report to" person listed on the data sheet. If you are unable to obtain the information before the samples must be submitted for testing, choose the code that seems most appropriate. Refer to the Chemistry Lab Handbook (and background information in this section) to aid you. The code can be changed once you obtain the correct information.

Make sure the station numbers, field numbers, sampling points and site ID's on the forms correspond with the information on the samples.

Compare the collection time on the bottle with the time listed on the data sheet. If there is a discrepancy, make note of it on the data sheet.

Compare the analysis codes requested with the bottles submitted. See step 6 for more detail on this.

DETERMINING THAT CORRECT BOTTLES WERE SUBMITTED FOR THE REQUESTED TESTS

Check the Analysis codes requested to be sure that all of the correct bottles have been submitted.

Refer to the bottle-type charts to make your determinations.

If you determine that the wrong bottles have been submitted, some substitutions can be made:
Thiosulfate Bacteriology bottles can be used for fluoride and nitrite, but not for nitrate or sulfate.
Non-thiosulfate Bacteriology bottles can be used for fluoride, nitrate, nitrite and sulfate.
General bottles can be used for nitrate, if sample is 2 days old or less.
Nutrient bottles can be used for nitrate (this is routinely done by the MPCA).
Free Cyanide and Total Cyanide bottles are interchangeable if there is adequate sample volume.
Other substitutions may be possible, check with the lab when incorrect bottles have been submitted.
In all cases above, check with the laboratory before submitting the sample and record a receiving comment that briefly describes the bottle substitution.

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

MPCA collectors rarely request code 327. The bacteriology codes they most commonly request are 310: fecal coliform and 311: fecal strep.

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

MPCA SAMPLE SIGN-IN PROCEDURE (SEE EXAMPLE OF DATA SHEET):

Most MPCA Data Sheets must be signed like a chain-of-custody form, even when the samples are not officially chain-of-custody. They use the following forms:
Standard MPCA form for water
Standard MPCA form for sediment
MPCA chain-of-custody form
MDH chain-of-custody form
MDH Organics Data Sheet
Forms from MPCA sub-contractors
The most common sub-contractors are Interpoll Labs, Conestoga-Rover and Foth & Van Dyke (the facilities that collect closed landfill samples).

The two standard MPCA forms are signed on the back of the white copy of the form. This is not strictly enforced, but if the collector or courier signs the form, then we should as well. The lab received date should also be recorded in the space provided on the front of the form, upper right.

The other forms are signed on the front of the top copy so that the information goes through all copies.

For all types of forms, the collector or courier will sign their name in the "relinquished by" column. They will also record the date and time of sample delivery.

A Sample Receiving employee must sign their name in the "received by" column, then record the date and time of sample acceptance.

## MPCA SAMPLE SCHEDULING

Some MPCA collectors send us samples on a routine basis while others send samples more sporadically. They are all supposed to inform us of any BOD, CBOD, Fecal Coliform, Fecal Strep, and Ortho Phosphorus samples they will be submitting. The most important samples to know when they are coming are the Fecal Coliform samples since they only have a 24 hour hold time. They should also inform us of any other unusual samples they will bring in, such as Chain of Custody or Priority One samples. They may notify us by phone, email or fax.

If a collector calls, ask them for the following information:
Collector Name
Date and time samples will arrive at MDH
Total number of samples
Analyses requested on each sample
Sample type (lake water, stream water, sediment, paint, etc)
Priority One/Chain of Custody Information

If they do not provide enough information in an email, fax or phone message, contact them for more detail.

Pass this information onto the lab by sending a "New Task" through GroupWise to the bactichem unit. Be sure and mark the correct day of delivery in the message.

Sandy Bissonette and Beth Endersbe of the MPCA collect water samples on a routine basis from the spring through the fall of each year. They provide us with their planned schedule ahead of time, usually via email. They frequently order BOD and Fecal Coliform tests. They collect these samples from six different routes (or loops).

## MPCA SAMPLE BOTTLE ORDERS

MPCA Warehouse Bottle Supply
The MPCA stocks their warehouse with MDH bacteriology, cyanide, metals, mercury, nutrient

and general (all 3 sizes) bottles. They fill most of their bottle orders from that supply. The MPCA courier (Ed Norwig) drops off and picks up bottle orders when he brings samples in.

Standing (Monthly) Bottle Orders
Periodically, Sandy Bissonette and Beth Endersbe send us their "standing" bottle order. Generally, Lab Services Shipping personnel fill these orders on a monthly basis. The MPCA courier picks up the orders and delivers them to the MPCA warehouse.

Specialized Bottle Orders
Local MPCA collectors frequently place more complicated and specialized bottle orders directly with us. Many of these orders are for emergencies and we try to fill them as needed. Most organic bottle orders are placed this way. If you are unsure what type of bottle the collector needs, refer them to the appropriate Unit Leader or other laboratory personnel for assistance.

Out-state Bottle Orders
Occasionally, out-state MPCA collectors place orders that they want shipped directly to them and we try to accommodate them. However, it the order is for a large number of routine bottles (general, nutrient, metal, cyanide, bacteriology etc), refer them to Ed Norwig in the MPCA warehouse.

# MPCA CLOSED LANDFILL PROGRAM

The Minnesota Pollution Control Agency (MPCA) administers this program in order to monitor the groundwater quality of sanitary landfills that are no longer in active use. The MPCA subcontracts with various private labs to collect the samples and deliver them to MDH for testing. We also provide sample bottles for these collectors.

We have standing (routine) bottle orders set up for some of the landfills that have a regular sampling schedule. The order information is in a yellow folder that is stored in a rack on the counter.

The parameter (test code) lists for these standing orders are in the desk file drawer, each in their own labeled folder. The parameter lists should be brought with the lab sheet every time.

Interpoll Labs faxes their bottle orders to us as needed. Their bottle orders list the parameters that will be run on the samples and we must determine the necessary bottles from this list. The parameter list is in alphabetical order, rather than by bottle type or numerical order. This makes it difficult to figure out the type of bottles needed when a person is new to sample receiving. Listed on the next page are the codes in the parameter list order with the bottle type listed by each code. A list of codes in numerical order follows, and finally a list of codes taken from each bottle type are listed.

| Alphabetical List | Test Code | Bottle type |
|---|---|---|
| Alkalinity | 22 | General 1 liter |
| Ammonia Nitrogen | 64 | Nutrient |
| Arsenic | 108/109 | Metals |
| Barium | 113/114 | Metals |
| BOD (bacti oxygen demand) | 96 | General 2 liter |
| Bromide (rarely ordered) | 455 | two 40 ml vials (ask organics) |
| Cadmium | 122/123 | Metals |
| Calcium | 694/695 | Metals |
| CBOD | 83 | General 2 liter |
| Chloride | 23 | General 1liter |
| Chromium | 129/130 | Metals |
| Cobalt | 136/137 | Metals |
| Copper | 145/146 | Metals |
| Iron | 152/154 | Metals |
| Lead | 157/158 | Metals |
| Magnesium | 696/697 | Metals |
| Manganese | 166/168 | Metals |
| Mercury | 200/202 | Mercury |
| Nickel | 171/172 | Metals |
| Nitrate (nitrate/nitrite) | 69 | Nutrient |
| Nitrite | 67 | General 1 liter |

| | | |
|---|---|---|
| Nitrogen (Ammonia) | 64 | Nutrient |
| Potassium | 255/256 | Metals |
| Sodium | 257/258 | Metals |
| Solids, total dissolved | 5 | General 1 liter |
| Solids, total suspended | 3 | General 1 liter |
| Sulfate | 28 | General 1 liter |
| Volatile Organic Compounds | 498 | 40 ml VOC vials |
| Vanadium | 248/249 | Metals |
| Zinc | 194/195 | Metals |

*Special dissolved analyses: Some of the metal and mercury samples will be filtered in the field. Make sure that you make note of which ones are filtered on the paperwork. The paperwork should be noted, but many times the paperwork is incorrect and it needs to be checked. When entering the analytical codes, make sure dissolved codes are entered in for the samples that were filtered. The parameter lists might not indicate what the dissolved codes are, so they will have to be look up in the Environmental Laboratory Handbook. This tends to take up a lot of time, so if there are any other samples that need to be delivered to the labs, do that before working on the Interpoll samples.

Numerical List

| **Analysis** | **Test Code** | **Bottle Type** |
|---|---|---|
| Solids, total suspended | 3 | General 1 liter |
| Solids, total dissolved | 5 | General 1 liter |
| Alkalinity | 22 | General 1 liter |
| Chloride | 23 | General 1 liter |
| Sulfate | 28 | General 1 liter |
| Phosphate (dissolved)* | 60 | Nutrient |
| Nitrogen (Ammonia) | 64 | Nutrient |
| Nitrite (total) | 67 | General 1 liter |
| Nitrate (total) | 69 | Nutrient |
| Nitrite (dissolved)* | 73 | General 125 ml |
| Nitrate (dissolved)* | 78 | Nutrient |
| CBOD | 83 | General 2 liter |
| BOD | 96 | General 2 liter |
| Arsenic | 108/109 | Metals |
| Barium | 113/114 | Metals |
| Cadmium | 122/123 | Metals |
| Chromium | 129/130 | Metals |
| Cobalt | 136/137 | Metals |
| Copper | 145/146 | Metals |
| Iron | 152/154 | Metals |

| | | |
|---|---|---|
| Lead | 157/158 | Metals |
| Manganese | 166/168 | Metals |
| Nickel | 171/172 | Metals |
| Zinc | 194/195 | Metals |
| Mercury | 200/202 | Mercury |
| Vanadium | 248/249 | Metals |
| Potassium | 255/256 | Metals |
| Sodium | 257/258 | Metals |
| Calcium | 694/695 | Metals |
| Magnesium | 696/697 | Metals |
| Bromide (rarely ordered) | 455 | 2 - 40 ml vials (ask organics) |
| VOC's | 498 | 3 VOC vials/set |

Parameter List by Bottle Type:

General 1 liter: 3, 5, 22, 23, 28, 67

General 125 ml: 73

General 2 liter: 83, 96

Metals: 108, 109, 113, 114, 122, 123, 129, 130, 136, 137, 145, 146, 152, 154, 157, 158, 166, 168, 171, 172, 194, 195, 248, 249, 255, 256, 257, 258, 694, 695, 696, 697

Mercury: 200, 202

Nutrient: 60, 64, 69, 78

VOC Vials: 498, 462 (3 vials for each code)

Tests not run at MDH: Sometimes there are parameters on the list that are not run at MDH but are analyzed by the collectors in the field. They are not assigned test codes on the parameter list (or by us).
These analyses are as follows:
Eh (mV), Iron II, Methane and Sulfide. Note that when Iron II is field analyzed, our lab must run Iron (codes 152/154). This may not be marked on the parameter list.

Cation-Anion Balance, Code 996: If this code is on a parameter list, do not enter it in the computer. It is a calculation that is done automatically when certain other tests are ordered.

Anoka Landfill Wetlands Samples: These are collected on a monthly basis, but Interpoll always faxes the order when needed; it is not a standing order done on a specific day. The order includes the parameter (analysis code) list. You can recognize the order by the sampling points: Cascade, Lift Station, Sed Basin, Splitter Tank, Manhole (MH)- 1AB, -2AB, -3AB, -4AB and MH-1BC, -2BC, -3BC, -4BC. This is a total of 12 sites, and they will need one set of VOC trip blanks.

BOD (code 96) and TSS (code 3) are run on these samples, so we give them 2 liter General bottles. We also provide Nutrient bottles and VOC vials for routine tests.

Therefore, the bottle order for this site is as follows:

12 Two liter General bottles
12 Metals bottles
12 Mercury bottles
12 Nutrient bottles
12 sets of VOC vials
1 set of VOC Trip Blanks

MPCA- BAYWEST

Meth Samples:
The samples from Baywest are usually Meth samples. The normal numbering procedure is still used. The program code for these samples is LG. The analysis code should be 484, which is the drug analysis code.

The distribution of the paperwork is however different. The paperwork is one of the three-page Chain of Custody forms. The pink copy goes to the collector. The yellow copy will be the one sent to Clerical. The white copy will be sent with the samples upstairs to the Organics Lab. They will keep a log book of the forms.

DRO Samples:
Baywest will bring in DRO samples for the Reserve Mining Project from time to time. Do not change the program code to LG. The pH of these samples will have to be checked and recorded on the pH verification sheet. A copy of this sheet will go with the samples and another one will go to Bill Scruton. The pH will have to be less than 2, so you might have to adjust as needed. When entering in the samples, a comment must be made for samples that are to be used for Matrix Spikes (MS) or Duplicate (MSD). This helps to notify the laboratory personnel that they have to do some spikes. Also put an orange dot with MS or MSD on the bottle. Deliver the samples to the Organics Laboratory with copies of the paperwork.

## MINNESOTA OSHA (LABOR AND INDUSTRY) SAMPLES

Minnesota OSHA is part of the State Labor and Industry Agency. They collect investigative samples from worksites as part of their response to complaints.

OSHA very rarely submits any water samples. Instead they submit:
Bulk samples for Metals and Asbestos
Carbon Air filters for solvents
Cartridge filters for formaldehyde
Cassette filters for Metals and Silica
Dust samples for Metals
Paint samples for Metals
Wipe samples for Metals
Other Miscellaneous samples.

THE PROGRAM CODE FOR ALL MN/OSHA SAMPLES IS MG.

The Data Sheet used for MN/OSHA samples does not have analysis code columns, nor does it have the Program Code printed anywhere. This makes it more difficult to process the samples because we have to look up the analysis codes for each set of samples that come in.

One section of the form has a list of Analytical Methods that looks like this:

Metals AAFL AAFU ICP
Solvents GC GC/MS HPLC
Asbestos Ph.C PLM TEM
Silica X-ray
Misc.

Analysts are supposed to circle the method they want and we use the information to help determine which analytical codes to assign and which Lab Unit should receive the samples.
Sometimes they write their analysis requests on the bottom of the form instead.
Solvent samples are for the Organics Lab.
Bactichem and Radiation rarely receive OSHA samples.

Metals: The Periodic Table of Elements Chemical Symbol of each Metal is listed after the name because OSHA collectors often request metals tests this way.

Metals Analysis Codes:

| | | |
|---|---|---|
| 653 | Aluminum | Al |
| 654 | Antimony | Sb |
| 655 | Arsenic | As |
| 656 | Barium | Ba |
| 657 | Beryllium | Be |

Metals Digest/Prep Codes:

| | |
|---|---|
| 682 | Miscellaneous |
| 683 | Filters |
| 684 | Wipes |
| 685 | Bulks |
| 686 | Dust |

| | | |
|---|---|---|
| 658 | Boron | B |
| 659 | Cadmium | Cd |
| 660 | Calcium | Ca |
| 661 | Chromium | Cr |
| 662 | Chromium, Hexavalent | Cr-6 |
| 663 | Cobalt | Co |
| 664 | Copper | Cu |
| 665 | Iron | Fe |
| 666 | Lead | Pb |
| 667 | Magnesium | Mg |
| 668 | Manganese | Mn |
| 669 | Mercury | Hg |
| 670 | Molybdenum | Mo |
| 671 | Nickel | Ni |
| 672 | Potassium | K |
| 673 | Selenium | Se |
| 674 | Silver | Ag |
| 675 | Sodium | Na |
| 676 | Thallium | Tl |
| 677 | Tin | Sn |
| 678 | Titanium | Ti |
| 679 | Vanadium | V |
| 680 | Zinc | Zn |
| 688 | Bismuth | Bi |

981 Formaldehyde, Cartridge: These samples must be sent to a private lab. They should be delivered to the metals unit.

687 Paint

One Digest/Prep Code must be assigned to each OSHA Metals sample along with the Analysis Codes.

If Metals Group 1 is requested, it consists of the following codes:

661 Chromium (+Insol. Salts)
664 Copper (fume, as Cu)
665 Iron (oxide fume)
668 Manganese (fume as Mn)
671 Nickel (+Insol. Comp.)
680 Zinc (oxide fume)

Organics Code:

597 Solvents (Air)

This code is assigned to all OSHA Organics samples. The following is a partial list of solvents that fall under this code:

Epichlorohydrin
Ethanol
Ethyl Benzene
Heptanon
Isobutyl Alcohol
Methylene Chloride
Petroleum Distillates
Stoddard Solvents
Toluene
Xylenes

We do not analyze for formaldehyde as a solvent but the Metals unit can run a different type of analysis for it. See metals codes on previous page.

Misc. Samples:
If there are no codes for the wanted tests (ex. Ozone) contact the assistant lab manager to set up subcontracting them to a different laboratory.

MINNESOTA OSHA SAMPLE PROCESSING PROCEDURE:
LABELING OSHA SAMPLES:

Do not remove the samples from their bags (the labs will do this).
Just clip the labels and paperwork to the bag containing the samples. The laboratory personnel will deal with labeling themselves.

MAKE A COPY OF THE DATA SHEET:

The copy is for the clerical unit.
Attach the original to the bag/labels.
The Metals Department wants the copy of the sheet to be delivered to them and the original to be sent to the Clerical Unit.

MISCELLANEOUS SAMPLES
PRIVATE WELL WATER TESTING

The only analysis that we do for private homeowners on a routine basis is the testing of new homeowner-drilled wells through the New Well Program. These samples should be accompanied by the appropriate paperwork.

We also test flooded well samples when there has been flooding in a given area of the state. In this case, we will be notified ahead of time that the Flooded Well Program has been activated and we should expect samples. These samples should also be accompanied by the appropriate paperwork.

All other private well testing must be pre-arranged through the Well Management program. In most cases, the homeowner will be directed to a local or county program for their testing needs.

Direct any inquiries to:

Well Management at 651-201- 4600 OR
Francine Lafayette at 651-201-4592

# Appendix C: MDH Environmental Laboratory Standard Operating Procedures

# QuikChem® Method 10-107-04-3-D

# DETERMINATION OF TOTAL NITROGEN IN WATERS BY IN-LINE DIGESTION FOLLOWED BY FLOW INJECTION ANALYSIS

## - IMIDAZOLE BUFFER METHOD -

**0.05 to 5.0 mg N/L Low Range**
**0.2 to 20.0 mg N/L High Range**

**(Method also includes Manifold Alterations to Analyze Nitrate/Nitrite)**

**Written by Scott Tucker**

**Applications Group**

**Revision Date:**

**2 December 2010**

**LACHAT INSTRUMENTS**
**5600 LINDBURGH DRIVE**
**LOVELAND, CO 80539 USA**

LACHAT INSTRUMENTS
A Hach Company Brand

**QuikChem® Method 10-107-04-3-D**

# Total Nitrogen, In-line Persulfate Digestion

## -Imidazole Buffer Method –

(Method also includes Manifold Alterations to Analyze Nitrate/Nitrite, see section 17.5)

**0.05 to 5.0 mg N/L**
**0.2 to 20.0 mg N/L**

## – Principle –

Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

## – Interferences –

1. Chloride is a suspected interference. Seawater, when spiked at 5 mg N/L as ammonia, gave < 5% recovery.

## – Special Apparatus –

Please see Parts and Price list for Ordering Information

1. Lachat Sample Preparation Module, A30X11 (X=1 for 110V, x=2 for 220V) with UV-254 lamp.
2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

# CONTENTS

# QuikChem® Method 10-107-04-3-D

# DETERMINATION OF TOTAL NITROGEN BY IN-LINE DIGESTION BY FLOW INJECTION ANALYSIS COLORIMETRY

## 1. SCOPE AND APPLICATION

1.1. Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

1.2. Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

1.3. After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

1.4. The method will recover nearly all forms of nitrogen. Nitrate and nitrite are recovered in this method. They are not recovered in the conventional Kjeldahl nitrogen method. Thus the resultant concentration for this method is termed total nitrogen and not Kjeldahl nitrogen.

1.5. The applicable range is 0.05 to 5.0 mg N/L for the low range and 0.2 to 20.0 mg N/L for the high range. The method detection limit is 0.003 mg N/L for the low range and 0.008 mg N/L for the high range. The method throughput is 45 injections per hour.

## 2. SUMMARY OF METHOD

2.1. Nitrogen compounds are oxidized in-line to nitrate using alkaline persulfate/UV digestion. Oxidation of nitrogen containing compounds to nitrate is achieved at 105°C with additional energy supplied by exposure to UV light. The digestion occurs prior to the injection valve.

2.2. Results for wastewater influent may be up to 30% low when compared with a rigorous TKN digestion because of sediment in the sample test tube. If effluent samples are preserved and filtered, in-line digestion results will match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

2.3. After digestion nitrate is quantitatively reduced to nitrite by passage of the sample through a copperized cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotization with sulfanilamide under acidic conditions to form a

diazonium ion. The diazonium ion is coupled with N-(1-naphthyl)ethylenediamine dihydrochloride. The resulting pink dye absorbs at 540 nm and is proportional to total nitrogen.

## 3. DEFINITIONS

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.1. ANALYTICAL BATCH -- The set of samples extracted/distilled/or digested at the same time to a maximum of 10 samples.

3.2. CALIBRATION BLANK (CB) -- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

3.3. CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4. FIELD BLANK (FMB) -- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a sample bottle holding time, preservatives, and all preanalysis treatments. The purpose is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.5. FIELD DUPLICATE (FD) -- Two samples taken at the same time and place under identical circumstances which are treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.6. LABORATORY BLANK (LRB) -- An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if the if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7. LABORATORY CONTROL STANDARD (LCS) -- A solution prepared in the laboratory by dissolving a known amount of one or more pure compounds in a known amount of reagent water. Its purpose is to assure that the results produced by the laboratory remain within the acceptable limits for precision and accuracy. (This should not be confused with a calibrating standard).

3.8. LABORATORY DUPLICATE (LD) -- Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

3.9. QUALITY CONTROL CHECK SAMPLE (QCS) -- A sample containing analytes of interest at known concentrations (true values) of analytes. The QCS is obtained for a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal preparation process.

3.10. METHOD DETECTION LIMIT (MDL) -- The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

## 4. INTERFERENCES

4.1. Chloride is a suspected interference.

## 5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

5.3.1. Cadmium

5.3.2. Sulfuric Acid

5.3.3. Phosphoric acid

5.3.4. Potassium persulfate

## 6. EQUIPMENT AND SUPPLIES

6.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1. Sampler

6.3.2. Multichannel proportioning pump

6.3.3. Reaction unit or manifold

6.3.4. Colorimetric detector

6.3.5. Data system

6.4. Special Apparatus

6.4.1. Lachat Sample Preparation Module, A30X11 (X=1 for 110V, x=2 for 220V) with UV-254 lamp.

6.4.2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD

## 7. REAGENTS AND STANDARDS

### 7.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

**Degassing with helium:** 5 min?

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 lb/in$^2$) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

**Reagent 1. Imidazole Buffer, pH ~ 7.4**

**By Volume:** In a **1L** volumetric flask, add ~ **600 ml** of **DI water**, **6.8 g** of **Imidazole** ($C_3H_4N_2$), and **2 ml** of **concentrated HCl** (it is recommended that addition of the HCl be carried out in a hood). Swirl to dissolve the imidazole and dilute to 1 L with DI water. The imidazole buffer was shown to be stable for at least one month.

**Reagent 2. Sulfanilamide Color Reagent**

**By Volume**: To a **1 L** volumetric flask add about **600 mL DI water**. Then add **100 mL 85% phosphoric acid** ($H_3PO_4$), **40.0 g sulfanilamide and 1.0 g N-(1-naphthyl)-ethylenediamine dihydrochloride** (NED). Shake to wet, and stir to dissolve for 30 minutes. Dilute to the mark with **DI water** and invert to mix. Store in a dark bottle and discard when the solution turns pink.

**By Weight:** To a tared, dark **1 L** container add **876 g DI water, 170 g 85% phosphoric acid ($H_3PO_4$), 40.0 g sulfanilamide**, and **1.0 g N-(1-naphthyl)ethylenediamine dihydrochloride** (NED). Shake until wetted and stir with a stir bar for 30 minutes until dissolved. Store in a dark bottle and discard when the solution turns pink.

**Reagent 3. Potassium Persulfate Oxidant**

43 of $Na_2S_2O_8$

**By Volume:** In a **1 L** volumetric flask containing approximately **900 mL water,** ~~add 49 g potassium persulfate~~ ($K_2S_2O_8$). Add **10 g disodium tetraborate decahydrate** ~~($Na_2B_4O_7 \cdot 10H_2O$).~~ Add a magnetic stir bar, dissolve and dilute to the mark with **DI water**. Invert to mix. Gentle heating or a warm water bath is required for complete dissolution.

potassium peroxodisulfate

**By Weight:** To a tared **1 L** container, add **975 g DI water** and **49 g potassium persulfate** ($K_2S_2O_8$). Add **10 g disodium tetraborate decahydrate** ($Na_2B_4O_7 \cdot 10H_2O$). Add a magnetic stir bar sir until dissolved. Gentle heating or a warm water bath is required for complete dissolution.

Potassium persulfate is known to have nitrogen contamination. There are two suggestions to reduce this contamination 1) re-crystallize the potassium persulfate, or 2) use sodium persulfate. If you choose to use sodium persulfate, use **43 g** of **$Na_2S_2O_8$** instead ~~of 49 g of $K_2S_2O_8$~~.

**Potassium persulfate re-crystallization procedure:**

1. Dissolve 100 g of potassium persulfate in approximately 600 ml of Milli-Q previously heated to 60° C. Use a medium sized stir bar and a 1000 mL flask.

2. Filter the solution rapidly through a sintered glass funnel.

3. Rinse the 1000 mL flask.

4. Poor filtrate back into the flask used to heat the potassium persulfate solution.

5. Cool solution to about 4° C by placing the flask in ice water. Whirl the flask continuously to prevent the solution from freezing.

6. Filter the 4° C solution and wash with 1 or 2 squeezes of ice cold Milli-Q, save the white solid.

7. Discard the filtrate from the sidearm flask.

8. Rinse the flask used to cool the solution with Milli-Q

9. Fill the flask with 450ml of Milli-Q and heat to 60° C.

10. Add the crystals from step 5 and mix into solution.

11. Repeat steps 4 and 5. The white granules on top of the filter are crystals!

12. Dry crystals in vacuo over anhydrous calcium chloride. Rapid drying in a good vacuum and thus at a low temperature is essential as this will minimize the sulfuric acid formation on the crystals.

The yield is about 80%. The effect is illustrated by the blank obtained in the standard procedure-0.178 for the original reagent, 0.02 after one re-crystallization and 0.01 µmole of N after two re-crystallizations.

**Reagent 4. Buffer Solution for Digestion**

**By Volume:** In a **1 L** volumetric flask dissolve **25.0 g disodium tetraborate decahydrate** ($Na_2B_4O_7 \cdot 10\ H_2O$) and **3.0 g sodium hydroxide** (NaOH) in approximately **900 mL water.** Adjust to pH = 9.0 with sodium hydroxide or hydrochloric acid. Add a magnetic stirbar, dissolve and dilute to the mark with **DI water**. Gentle heating may be required for complete dissolution. Invert to mix.

## 7.2. PREPARATION OF STANDARDS

To prepare the stock and working standards, the following containers will be required:

**By Volume:** Two 1 L volumetric flasks and seven 250 mL volumetric flasks.

**By Weight:** Two 1 L containers and seven 250 mL containers.

**Standard 1. Stock Standard 1000 mg N/L**

In a **1 L volumetric flask** dissolve **7.221 g potassium nitrate** ($KNO_3$), pre-dried (60°C for 1 hour) or **4.93 g sodium nitrite** ($NaNO_2$) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. When refrigerated the nitrate standard may be stored for up to three months. Standards prepared as nitrate are more stable than those prepared as nitrite.

**Standard 2. 100.0 mg N/L**

**By Volume:** In a **1 L** volumetric flask add **100 mL of Standard 1** (1000 mg N/L). Dilute to the mark with **DI water** invert to mix. Prepare fresh weekly.

### Standard 3. 10.0 mg N/L

**By Volume:** In a **1 L** volumetric flask add **10 mL of Standard 1** (1000 mg N/L). Dilute to the mark with **DI water** invert to mix. Prepare fresh weekly.

### Low Range Standards

| **Working Standards** (Prepare Daily)<br><br>Concentration mg N/L | **A**<br><br>5.00 | **B**<br><br>2.00 | **C**<br><br>1.00 | **D**<br><br>0.40 | **E**<br><br>0.20 | **F**<br><br>0.10 | **G**<br><br>0.05 | **H**<br><br>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**<br><br>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)<br><br>Concentration mg N/L | **B**<br><br>20.0 | **C**<br><br>10.0 | **D**<br><br>5.00 | **E**<br><br>2.00 | **F**<br><br>1.00 | **G**<br><br>0.40 | **H**<br><br>0.20 | **I**<br><br>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**<br><br>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**<br>Divide exact weight of the standard by this **factor** to give final weight | 0.005 |

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (maximum of 2 mL concentrated $H_2SO_4$ per liter) and refrigerated. **CAUTION:** Samples must not be preserved with mercuric chloride or thiosulfate because this will degrade the cadmium column.

8.2. Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis (if required), and minimize waste disposal.

## 9. QUALITY CONTROL

9.1. Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.1.1. Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in section 9.3.

9.1.2. Analyses of laboratory blanks are required to demonstrate freedom from contamination.

9.1.3. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision and recovery sample that the analysis system is in control.

9.1.4. The laboratory should maintain records to define the quality of data that is generated.

9.2. INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1. Method Detection Limit (MDL) --To establish the ability to detect the analyte, the analyst shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in section 1.2 must be achieved prior to the practice of this method.

9.2.2. Initial Precision and Recovery -- To establish the ability to generate acceptable precision results, the operator shall perform 10 replicates of a mid-range standard, according to the procedure beginning in Section 11.

9.2.2.1. Using the results of the replicates compute the average percent recovery (X) and the standard deviation (s) for the analyte. Use the following equation for the calculation of the standard deviation.

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

Where, n = Number of samples, x = concentration in each sample

9.2.2.2. Compare s and x results with the corresponding data in Section 17. If the results meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If however, s and x do not match the data in Section 17, system performance is unacceptable. In this event correct the problem, and repeat the test.

9.3. Matrix spikes- The laboratory must spike, in duplicate, a minimum of 10 percent of all samples (one sample in each batch of ten samples) from a given sampling site or if for compliance monitoring, from a given discharge. The two sample aliquots shall be spiked with the stock standard (section 7.2).

9.3.1. The concentration of the spike in the sample shall be determined as follows:

9.3.1.1. If, as in compliance monitoring, the concentration of the analyte in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), which ever is higher.

9.3.1.2. If the concentration of the analyte in a sample is not being checked against a limit, the spike shall be at the concentration of the precision and recovery standard used in Section 9.2.5 or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2. Analyze one sample aliquot out of each set of ten samples from each site or discharge according to the procedure beginning in Section 11 to determine the background concentration of (B) of the analyte.

9.3.2.1. If necessary, prepare a standard solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2. Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A)

9.3.3. Calculate the percent recovery (P) of the analyte in each aliquot using the following equation.

$$P = \frac{(A - B)100}{T}$$

Where, A = Measured concentration of analyte after spiking, B = measured background concentration of analyte, T = True concentration of the spike

9.3.4. The percent recovery of the analyte should meet current laboratory acceptance criteria.

9.3.4.1. If the results of the spike fail the acceptance criteria and the recovery of the QC standard in the ongoing precision and recovery test of the analytical batch is within the current laboratory acceptance criteria, an interference is present. In this case, the results may not be reported for regulatory compliance purposes and the analyst must assess the potential cause for the interference. If the interference is attributable to sampling, the site or discharge should be resampled. If the interference is attributable to a method deficiency, the analyst must modify the method, repeat the test required in Section 9.1.2 and repeat the analysis of the sample and the matrix spike.

9.3.4.2. If the results of both the spike and ongoing precision and recovery test fail the acceptance criteria, the analytical system is judged to be out of control, and the problem shall be identified and corrected, and the sample reanalyzed.

9.3.5. Compute the relative percent difference (RPD) between two sample results using the following equation:

$$RPD = \frac{(D_1 - D_2)}{(D_1 + D_2)/2} \times 100$$

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

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

9.4. Laboratory blanks - Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1. Analyze a laboratory reagent water blank initially (with the test in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2. If analyte is detected in the blank at a concentration greater than MDL (Section 3.10.), analysis of the samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.

9.5. Calibration Verification Verify calibration using the procedure described in Section 10

9.6. On-going Precision and Recovery (OPR) - With every analytical batch, a midrange standard must be prepared using the procedure described in Section 11.

9.6.1. Compare the results with the current laboratory acceptance criteria. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed.

9.7. Quality Control Samples (QCS) It is suggested that the laboratory obtain and/or prepare a quality control sample using a source different from the source routinely used in Section 7. The QCS is used to verify the concentrations of the calibration standards.

9.8. Depending on the specific program requirements, field replicates and field spikes of the analytes of interest into samples may be required to assess the precision and accuracy of the sampling and sample transporting techniques.

## 10. CALIBRATION AND STANDARDIZATION

10.1. Prepare reagents and standards as described in Section 7.

10.2. Set up manifold as shown in Section 17.

10.3. Input data system parameters as shown in Section 17.

10.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

10.5. Place standards in the sampler. Input the information required by the data system.

10.6. Calibrate the instrument by injecting the standards. The data system will then associate the concentrations with the peak area for each standard to determine the calibration curve.

10.7. Verify calibration using a midrange calibration standard every ten samples or every analytical batch. Compute the percent recovery using the following equation:

$$\%recovery = \frac{D}{K} \times 100$$

Where, D = Determined concentration of analyte in the calibration standard, K = Actual concentration of the analyte in the calibration standard

10.8. If % recovery exceeds +/-10%, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected and the analytical batch reanalyzed

## 11. PROCEDURE

### 11.1. SAMPLE PRETREATMENT - PROCEDURE

11.1.1. Samples may be determined without preservation or preserved with sulfuric acid as directed above.

11.1.2. Both standards and samples should be carried through this procedure. If samples have been preserved with sulfuric acid, standards should be preserved in the same manner.

11.1.3. Samples may be homogenized in a device designed for this purpose. However, turbid samples should be filtered since the digestion effectiveness on nitrogen containing particles is unknown.

### 11.2. CALIBRATION PROCEDURE

11.2.1. Prepare reagent and standards as described in Section 7.

11.2.2. Set up manifold as shown in Section 17.

11.2.3. Input data system parameters as shown in Section 17.

11.2.4. Pump DI water through all reagent lines and check for leaks and smooth flow. Switch to reagents and allow the system to equilibrate until a stable baseline is achieved.

11.2.5. Place samples and/or standards in the sampler. Input the information required by the data system, such as concentration, replicates and QuikChem scheme (See Section 17).

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

### 11.3. SYSTEM NOTES

11.3.1. For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual. This guide is also available on request from Lachat.

11.3.2. Allow more than 20 minutes for the heating unit in the sample prep module to warm to 105°C. Tubing crimp formation has been observed in the past with the PTFE manifold tubing when no liquid is running through heater tubing and the tubing is allowed to bake. Running liquid through the heater whenever the temperature is above 80°C is necessary.

11.3.3. Since the digestion occurs prior to injecting the sample and since there is an air segment between the sample and the sampler wash solution, the valve and sample timing parameters are critical. It is important to verify that the center of the sample zone is injected.

11.3.4. Because the blank peak in this method is due to nitrogen in the buffer and persulfate solid reagents, it is important to use the best purity available.

11.3.5. Digestion efficiency should be verified by determining non-nitrate standards at regular intervals. A good plan is to use urea and nicotinic acid. Urea recovery

goes down when the digestion is too rigorous and nicotinic acid requires optimal functioning of all digestion parameters for recovery >95%.

11.3.6 To prevent ammonium contamination during system start up and shut down, use a separate wash vessel dedicated to the ammonium chloride buffer.

11.3.7 It is advisable to periodically determine a nitrite standard to check column efficiency. If column efficiency is < 90% replace the column.

11.3.8 System Maintenance for best results:

11.3.8.1. Change PVC tubing every three days.

11.3.8.2. Change tubular membrane of debubbler every two days. (The membranes in the alternate debubbler are changed only as required, and may last 3-4 weeks or more).

11.3.8.3. Change cadmium column every 200 samples.

11.3.9 Check list before running real samples.

11.3.9.1. Check that the method's timing has been correctly set by running food dye (bypass cadmium column at this time).

11.3.9.2. Check the temperature of digestion module (105° for TN and 125° for TP)

11.3.9.3. Check that all reagents are prepared correctly, to ensure there is no precipitation in the digestion buffer solution.

11.3.9.4. Check that the debubbler is in good condition, and it is efficiently debubbling by running one duplicate standard. (Cadmium column should be in correct position for TN). Please note that there may condensation at the outlet of the alternate debubbler. A true leak occurs around the edge of the disc with this debubbler. 7.3.9.5. Check that the cadmium column is in good condition by looking at the color. The color of cadmium should be black or dark gray. If white precipitated material is seen in the column, replacement is necessary.

11.3.9.6. If acceptable, duplicate peaks are produced, real samples can be run. Otherwise adjust the timing and troubleshoot or perform maintainence on the system until it is in good condition.

## 12. DATA ANALYSIS AND CALCULATIONS

12.1. Calibration is done by injecting standards. The data system will then prepare a calibration curve by plotting response versus standard concentration. Sample concentration is calculated from the regression equation.

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

12.3. Report results in mg N/L.

## 13. METHOD PERFORMANCE

13.1. The method support data are presented in Section 11. This data was generated according to a Lachat Work Instruction during development of the method.

13.2. Although Lachat Instrument publishes method performance data, including MDL, precision, accuracy and carryover studies, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions, as well as laboratory technique play a major role in determining method performance. The support data serves as a guide of the potential method performance. Some labs may not be able to reach this level of performance for various reasons, while other labs may exceed it.

## 14. POLLUTION PREVENTION

14.1. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the United States Environmental Agency (USEPA) recommends recycling as the next best option.

14.2. The quantity of chemicals purchased should be based on expected usage during their shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3. For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

## 15. WASTE MANAGEMENT

15.1. It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operation. Compliance with all sewage discharge permits and regulations is also required.

15.2. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N. W., Washington D. C. 20036, (202) 872-4477.

## 16. REFERENCES

16.1. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes. EPA-600/R-93/100, Revised August 1993, Method 353.2.

16.2. Determination of Nitrogen in Water: Comparison of a Continuous-flow method with on-line UV Digestion with the original Kjeldahl method, Hennie Kroon, Analytica Chemica Acta, 276, (1993) 287-293.

16.3 Lachat Instruments Inc., QuikChem Method 10-107-04-3-P.

# 17. TABLE, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

## 17.1. DATA SYSTEM PARAMETERS FOR QUIKCHEM 8000/8500

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

| | |
|---|---|
| Sample throughput: | 40 samples/h, 90 s/sample |
| Pump Speed: | 35 |
| Cycle Period: | 90 |

**Analyte Data:**

| | |
|---|---|
| Concentration Units: | mg N/L |
| Peak Base Width: | 42 s |
| Inject to Peak Start: | 30.8 s |
| Chemistry: | Direct/Bipolar |

**Calibration Data:**

**Low Range**

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Concentration mg N/L | 5.00 | 2.00 | 1.00 | 0.40 | 0.20 | 0.10 | 0.05 | 0.00 |

**High Range**

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Concentration mg N/L | 20.0 | 10.0 | 5.00 | 2.00 | 1.00 | 0.40 | 0.20 | 0.00 |

| | |
|---|---|
| Calibration Rep Handling: | Average |
| Calibration Fit Type: | 2nd Order Polynomial |
| Weighting Method: | 1/x |
| Force through zero: | No |

**Sampler Timing:**

| | |
|---|---|
| Min. Probe in Wash Period: | 19 s |
| Probe in Sample Period: | 60 s |

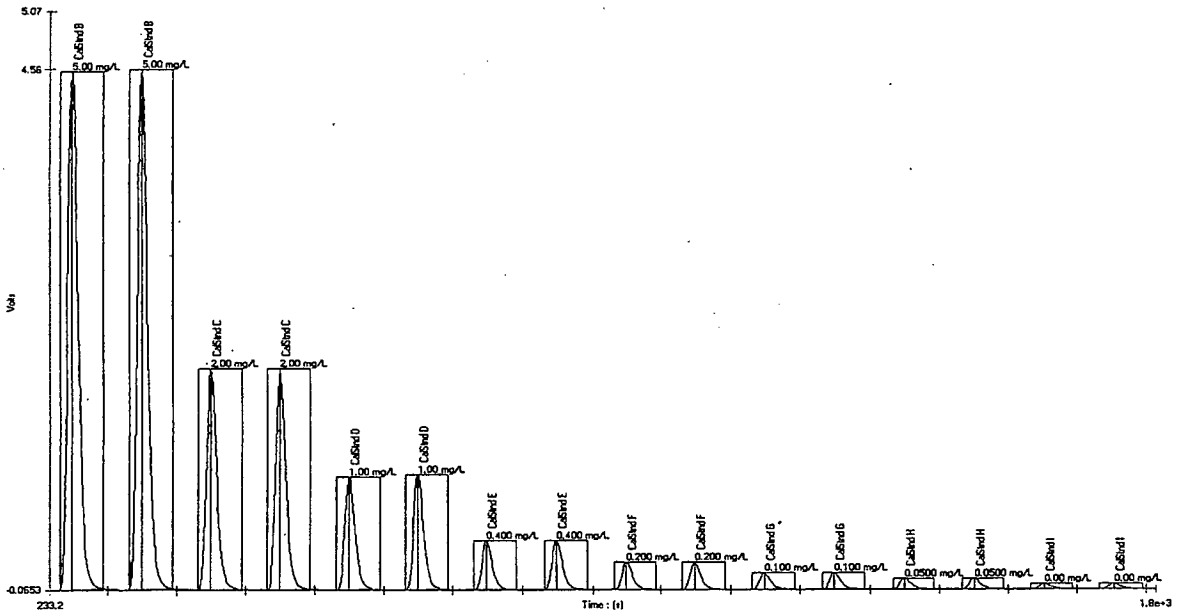
**Valve Timing:**

| | |
|---|---|
| Load Period: | 30 s |
| Inject Period: | 60 s |
| Sample Reaches 1st Valve | 160 s* |

*The time it takes the sample to reach the valve needs to be timed for the specific manifold being utilized. The time listed is just a starting point. The best way to calculate the time to valve is as follows: When the sampler probe travels to the sample, it will draw up an air slug. Start timing when the sampler probe goes into the sample, then watch the air slug travel through the heater, then out of the UV lamp. Once it reaches the debubbler stop timing, and add 5 to 10 seconds for the beginning of the sample slug to reach the valve. This recorded time with the additional 5 to 10 seconds added will be the time that should be entered in the software as the sample reaches first valve.

## 17.2. SUPPORT DATA FOR QUIKCHEM 8000/8500

### Calibration Data for Total Nitrogen Low Range



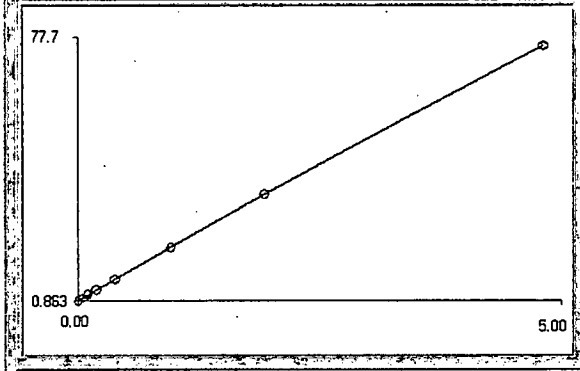

File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

### Calibration Graph and Statistics

Calibration Results - Channel 1

TN

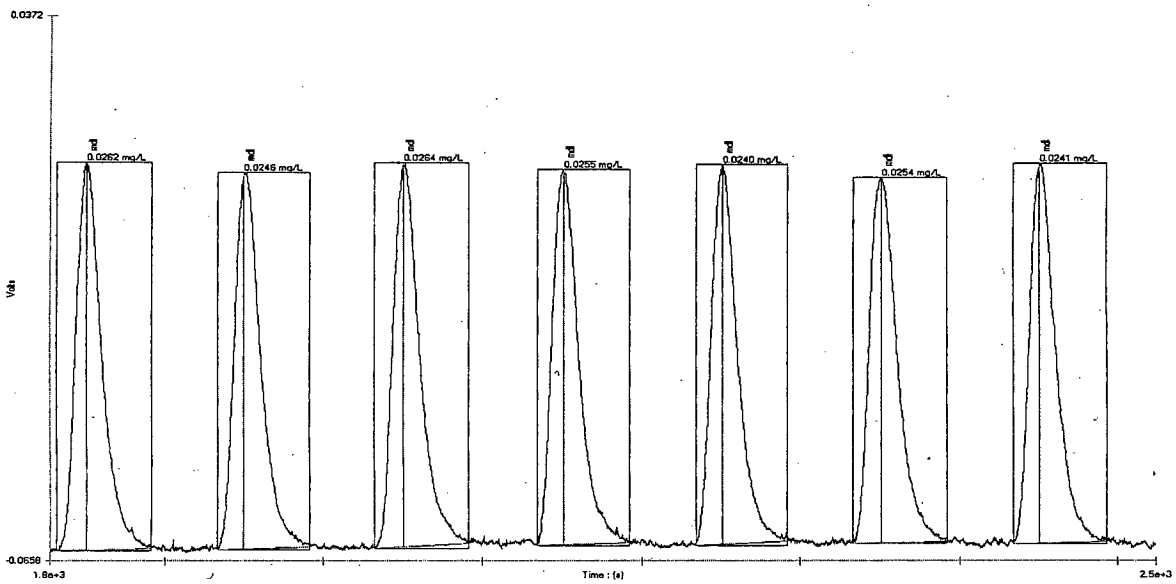
| | Known Conc. (mg/L) | Rep. | Peak Area (V.s) | Peak Height (V) | % RSD | % Resid. | Unused | Det. Conc (mg/L) | Date | Time |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5.00 | 1 | 77.4 | 4.60 | 0.3 | 0.2 | ☐ | 4.99 | 11/19/2007 | 12:52:36 PM |
| 2 | 5.00 | 2 | 77.7 | 4.62 | 0.3 | -0.2 | ☐ | 5.01 | 11/19/2007 | 12:54:14 PM |
| 3 | 2.00 | 1 | 32.9 | 1.98 | 0.3 | -0.7 | ☐ | 2.01 | 11/19/2007 | 12:55:52 PM |
| 4 | 2.00 | 2 | 32.8 | 1.97 | 0.3 | -0.2 | ☐ | 2.01 | 11/19/2007 | 12:57:30 PM |
| 5 | 1.00 | 1 | 16.9 | 1.01 | 0.6 | 0.8 | ☐ | 0.991 | 11/19/2007 | 12:59:08 PM |
| 6 | 1.00 | 2 | 16.7 | 1.03 | 0.6 | 1.6 | ☐ | 0.982 | 11/19/2007 | 1:00:45 PM |
| 7 | 0.400 | 1 | 7.44 | 0.441 | 0.4 | -0.6 | ☐ | 0.402 | 11/19/2007 | 1:02:22 PM |
| 8 | 0.400 | 2 | 7.40 | 0.437 | 0.4 | 0.0 | ☐ | 0.400 | 11/19/2007 | 1:04:03 PM |
| 9 | 0.200 | 1 | 4.11 | 0.243 | 1.1 | 1.2 | ☐ | 0.197 | 11/19/2007 | 1:05:42 PM |
| 10 | 0.200 | 2 | 4.18 | 0.244 | 1.1 | -0.4 | ☐ | 0.201 | 11/19/2007 | 1:07:18 PM |
| 11 | 0.100 | 1 | 2.59 | 0.147 | 0.3 | -2.2 | ☐ | 0.103 | 11/19/2007 | 1:08:57 PM |
| 12 | 0.100 | 2 | 2.58 | 0.147 | 0.3 | -1.8 | ☐ | 0.103 | 11/19/2007 | 1:10:36 PM |
| 13 | 0.0500 | 1 | 1.77 | 0.0970 | 1.3 | -2.4 | ☐ | 0.0526 | 11/19/2007 | 1:12:13 PM |
| 14 | 0.0500 | 2 | 1.74 | 0.0949 | 1.3 | -0.6 | ☐ | 0.0507 | 11/19/2007 | 1:13:52 PM |
| 15 | 0.00 | 1 | 0.863 | 0.0456 | | | ☐ | -2.86e-3 | 11/19/2007 | 1:15:30 PM |
| 16 | 0.00 | 2 | 0.874 | 0.0470 | | | ☐ | -2.16e-3 | 11/19/2007 | 1:17:07 PM |




Area = -0.190 * Conc^2 + 16.3 * Conc + 0.912
Conc = 5.13e-5 * Area^2 + 0.0612 * Area - 0.0557
Correlation Coefficient (r) = 0.99999

Weighting : 1/x

Settings



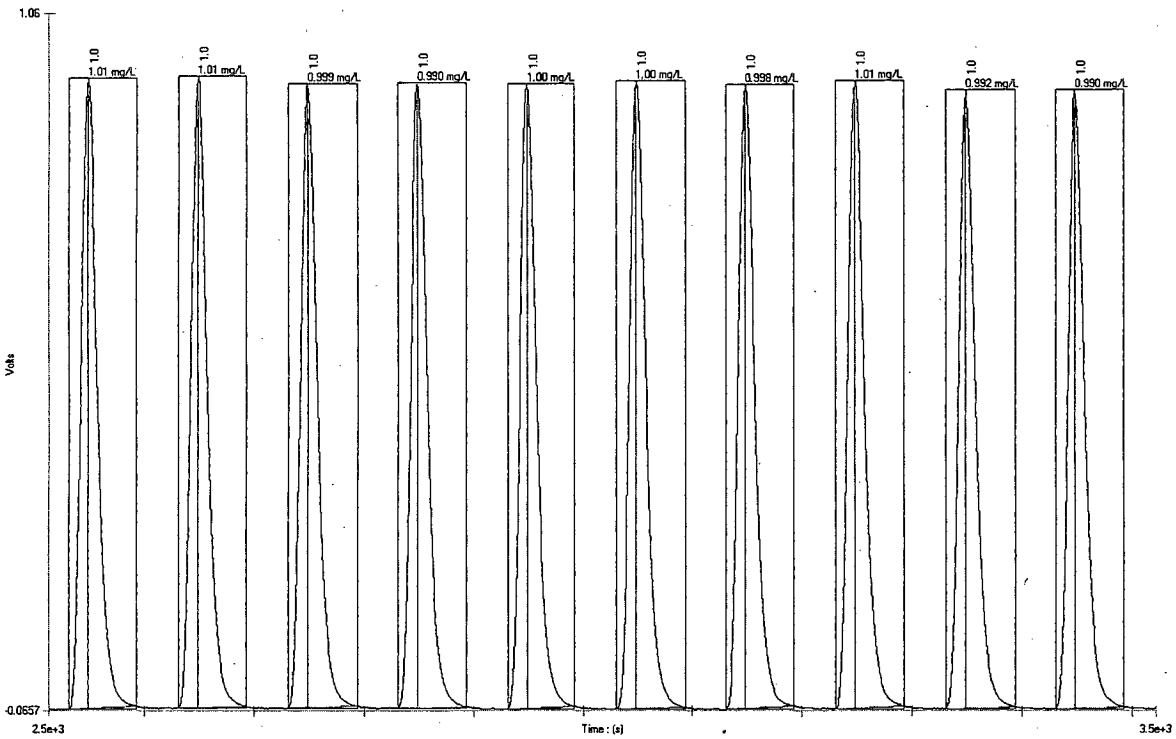

Method Detection Limit for Nitrogen using a 0.02 mg N/L standard

**MDL= 0.003 mg N/L**

Standard Deviation (s) = 0.00096 mg N/L, Mean (x) = 0.025 mg N/L, Known Value = 0.02 mg N/L

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

Acq. Date: 19 Nov 2007



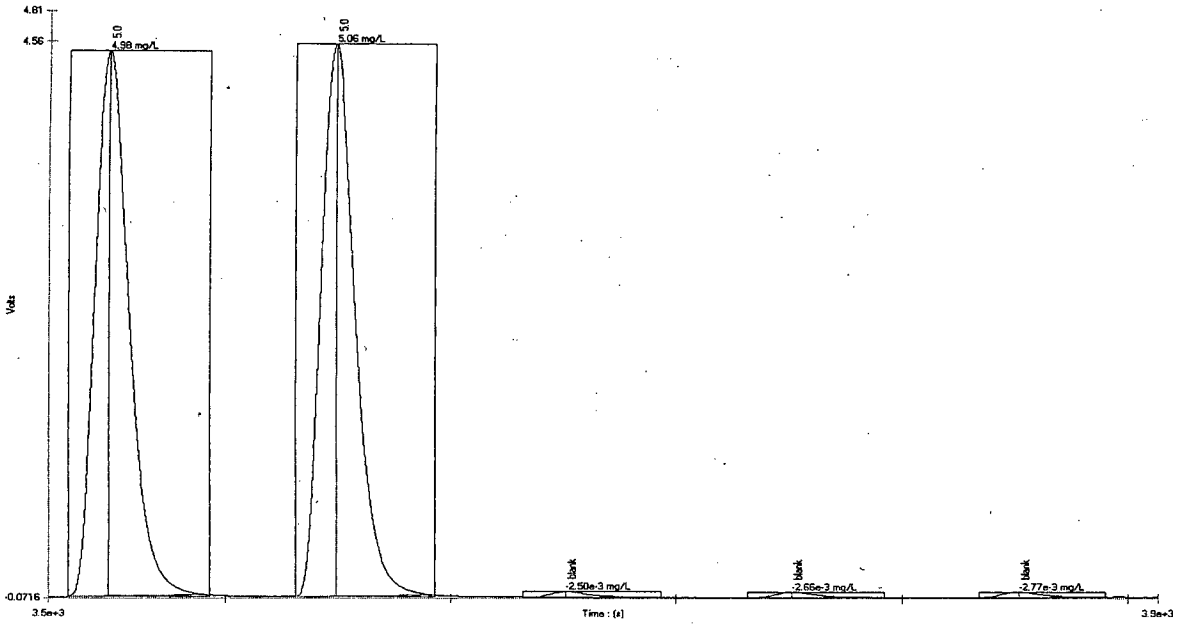

Precision Data for Nitrogen using a 1.0 mg N/L standard

**% RSD =0.75**

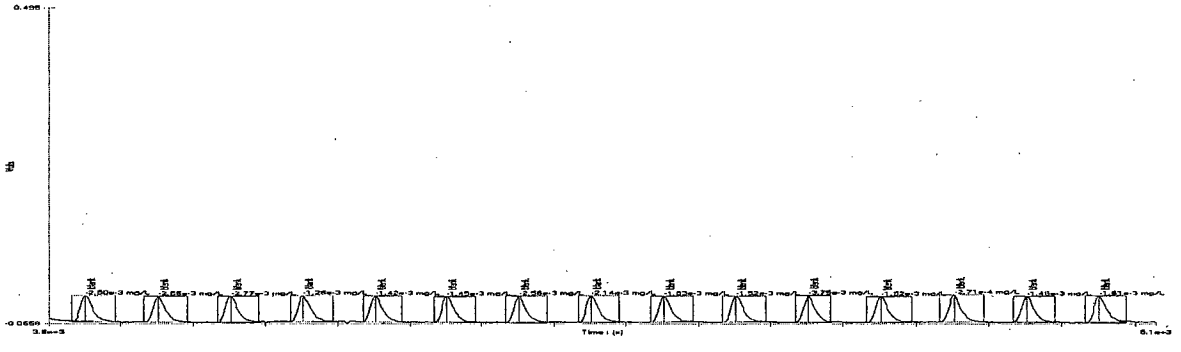
Standard Deviation (s) = 0.0075 mg N/L, Mean (x) = 1.00 mg N/L, Known Value = 1.00 mg N/L

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

Acq. Date: 19 Nov 2007




Carryover Study:
Two 5.0 mg N/L standards followed by three blanks
**Carryover Passed**
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007



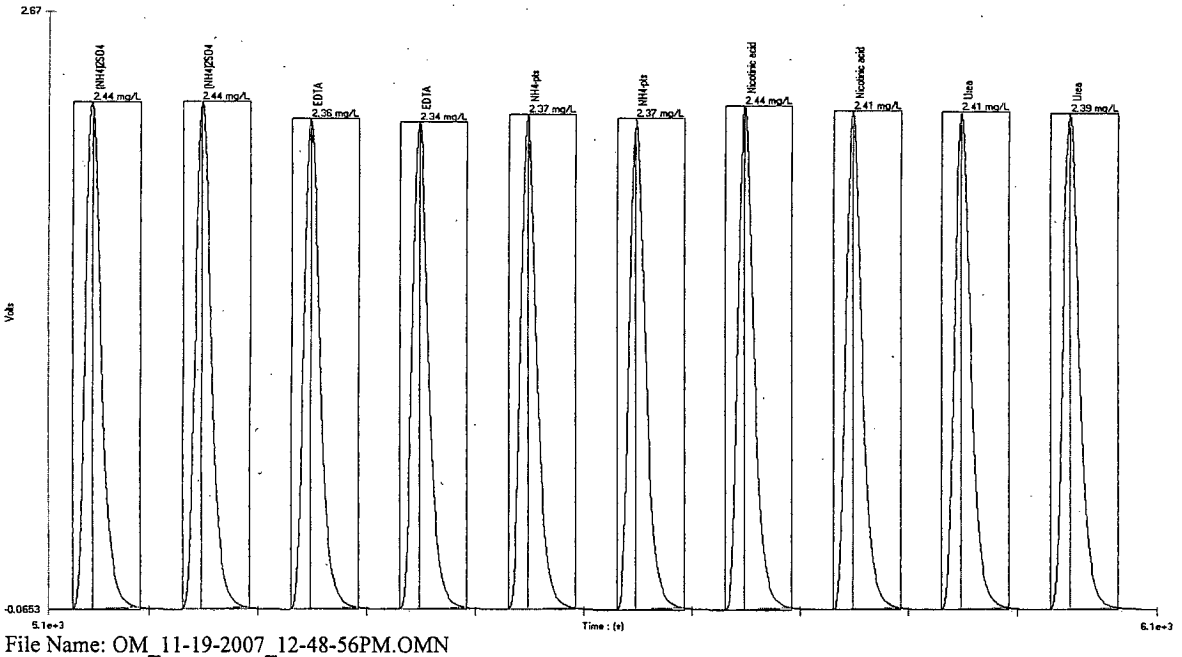
## DIN Blanks

Average: -0.00191 mg N/L, SD = 0.00083 mg N/L. Calculated DIN Limits: Detection Limit = 0.0025 mg N/L, Decision Limit = 0.005 mg N/L, Determination Limit = 0.0075 mg N/L.
File Name: OM_11-19-2007_12-48-56PM.OMN
Acq. Date: 19 Nov 2007

Digestion Efficiency for Nitrogen containing compounds in DI water at 2.5 mg N/L

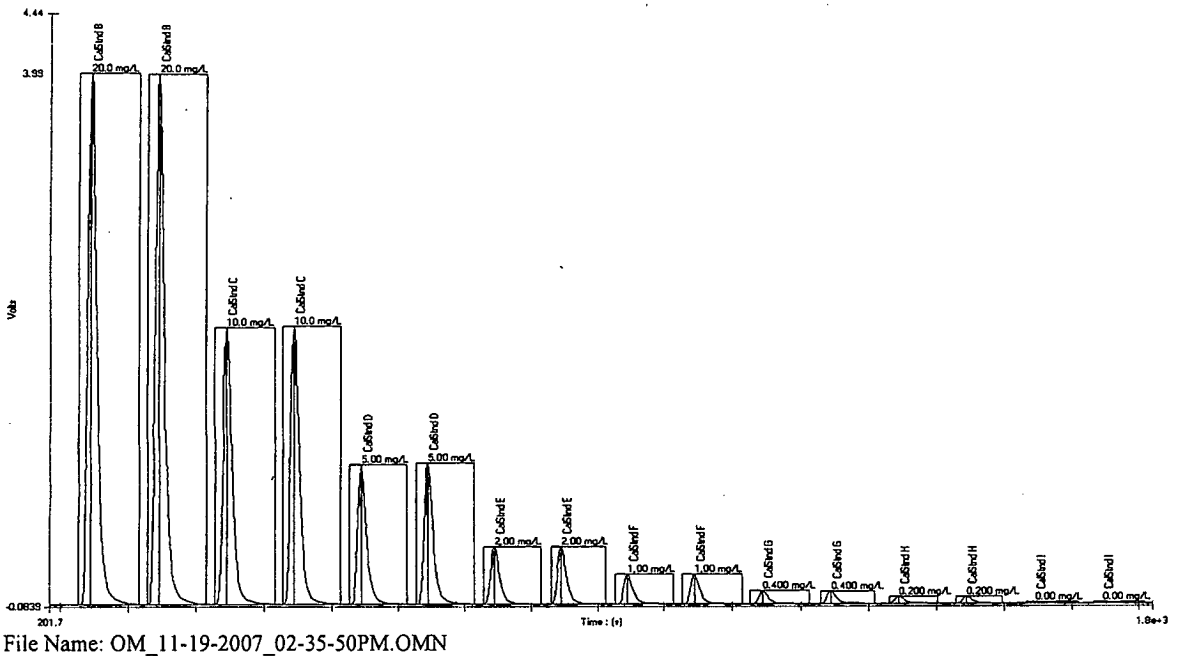
| Nitrogen Form | Mean Result (mg N/L) | %Recovery |
|---|---|---|
| Ammonia | 2.44 | 97.6 |
| EDTA | 2.35 | 94.0 |
| NPTS* | 2.37 | 94.8 |
| Nicotinic Acid | 2.43 | 97.0 |
| Urea | 2.40 | 96.0 |

* Ammonium p-toluenesulfonate




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

## Calibration Data for Total Nitrogen High Range



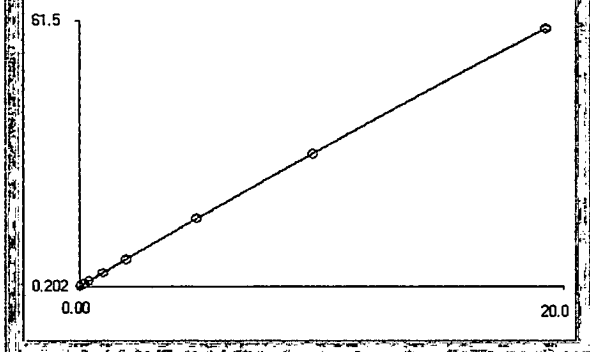

File Name: OM_11-19-2007_02-35-50PM.OMN
Acq. Date: 19 Nov 2007

## Calibration Graph and Statistics

Calibration Results - Channel 1

TN

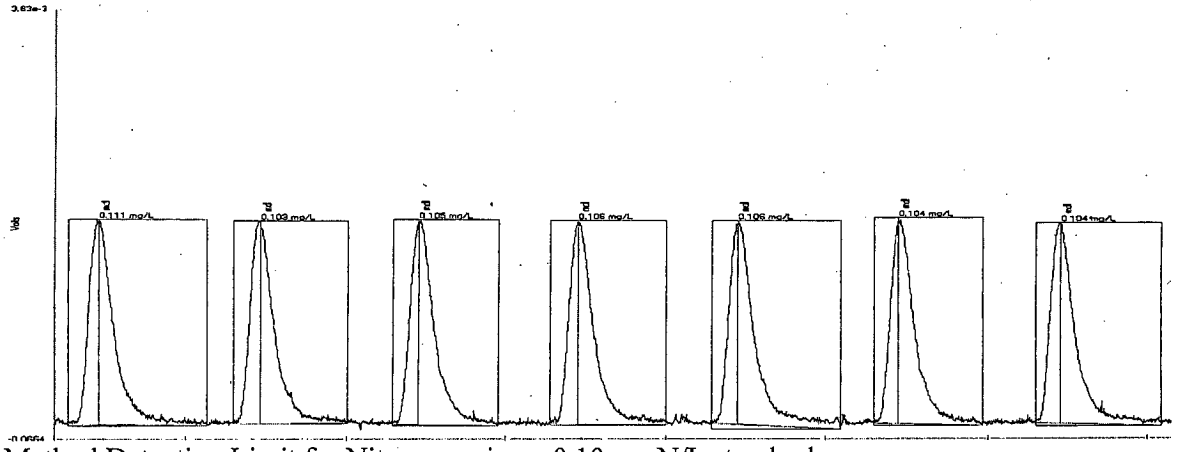
| | Known Conc. (mg/L) | Rep. | Peak Area (V.s) | Peak Height (V) | % RSD | % Resid. | Unused | Det. Conc (mg/L) | Date | Time |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20.0 | 1 | 61.5 | 4.05 | 0.3 | -0.2 | ☐ | 20.0 | 11/19/2007 | 2:39:32 PM |
| 2 | 20.0 | 2 | 61.2 | 4.05 | 0.3 | 0.2 | ☐ | 20.0 | 11/19/2007 | 2:41:10 PM |
| 3 | 10.0 | 1 | 31.7 | 2.11 | 0.1 | 0.3 | ☐ | 9.98 | 11/19/2007 | 2:42:47 PM |
| 4 | 10.0 | 2 | 31.8 | 2.12 | 0.1 | 0.1 | ☐ | 10.0 | 11/19/2007 | 2:44:25 PM |
| 5 | 5.00 | 1 | 16.3 | 1.07 | 0.6 | -0.2 | ☐ | 5.01 | 11/19/2007 | 2:46:03 PM |
| 6 | 5.00 | 2 | 16.4 | 1.08 | 0.6 | -1.1 | ☐ | 5.05 | 11/19/2007 | 2:47:41 PM |
| 7 | 2.00 | 1 | 6.66 | 0.441 | 1.1 | 0.5 | ☐ | 1.99 | 11/19/2007 | 2:49:17 PM |
| 8 | 2.00 | 2 | 6.56 | 0.437 | 1.1 | 2.0 | ☐ | 1.96 | 11/19/2007 | 2:50:54 PM |
| 9 | 1.00 | 1 | 3.48 | 0.228 | 0.3 | -0.4 | ☐ | 1.00 | 11/19/2007 | 2:52:31 PM |
| 10 | 1.00 | 2 | 3.49 | 0.229 | 0.3 | -0.9 | ☐ | 1.01 | 11/19/2007 | 2:54:08 PM |
| 11 | 0.400 | 1 | 1.56 | 0.0991 | 2.8 | -3.5 | ☐ | 0.416 | 11/19/2007 | 2:55:46 PM |
| 12 | 0.400 | 2 | 1.50 | 0.0970 | 2.8 | 0.6 | ☐ | 0.397 | 11/19/2007 | 2:57:25 PM |
| 13 | 0.200 | 1 | 0.851 | 0.0538 | 0.2 | 1.1 | ☐ | 0.197 | 11/19/2007 | 2:59:04 PM |
| 14 | 0.200 | 2 | 0.854 | 0.0541 | 0.2 | 0.8 | ☐ | 0.198 | 11/19/2007 | 3:00:42 PM |
| 15 | 0.00 | 1 | 0.211 | 0.0112 | | | ☐ | 1.42e-3 | 11/19/2007 | 3:02:20 PM |
| 16 | 0.00 | 2 | 0.202 | 0.0111 | | | ☐ | -1.27e-3 | 11/19/2007 | 3:03:59 PM |




Area = -0.0104 * Conc^2 + 3.26 * Conc + 0.208
Conc = 3.53e-4 * Area^2 + 0.305 * Area - 0.0631
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



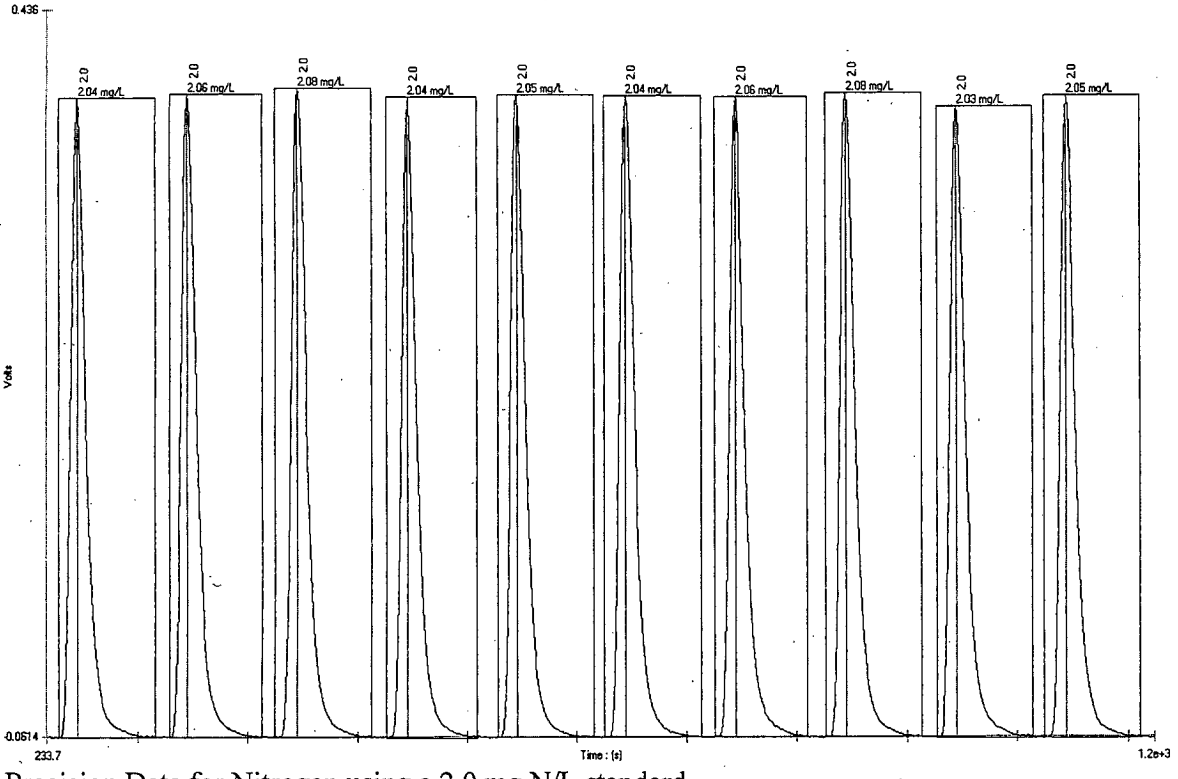
Method Detection Limit for Nitrogen using a 0.10 mg N/L standard

**MDL= 0.008 mg N/L**

Standard Deviation (s) = 0.0026 mg N/L, Mean (x) = 0.106 mg N/L, Known Value = 0.10 mg N/L

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

Acq. Date: 19 Nov 2007



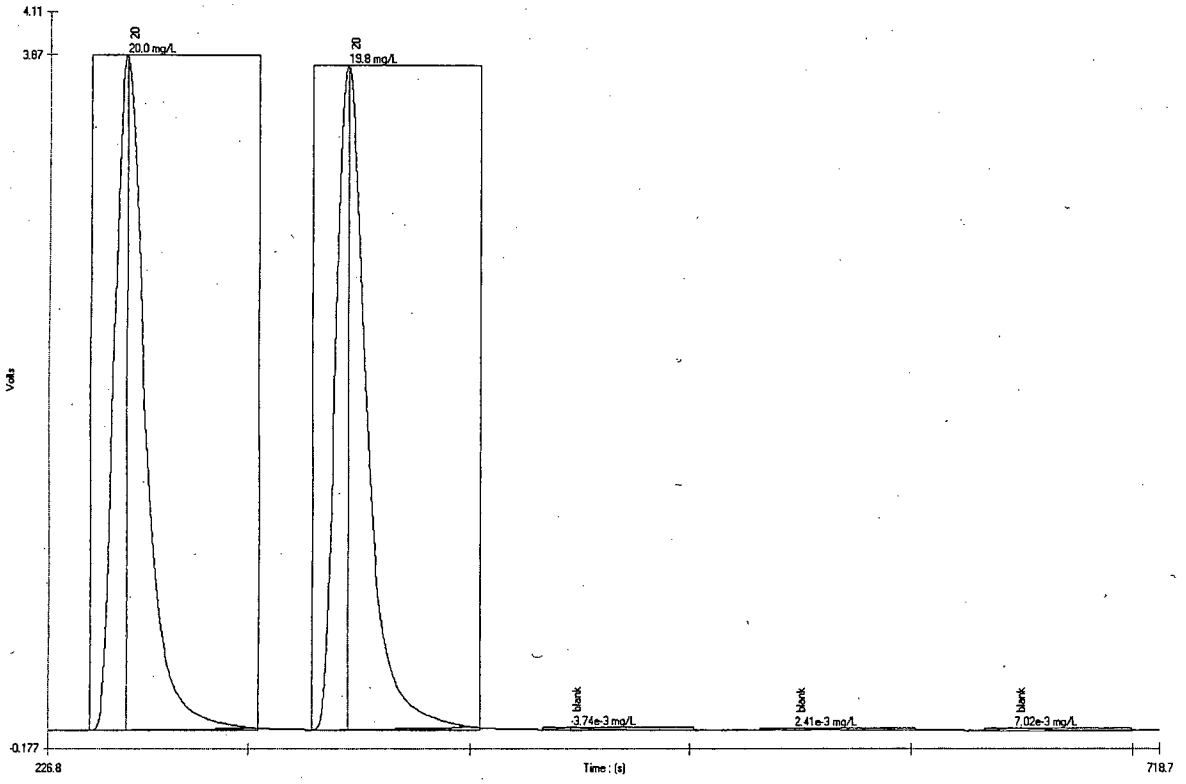

Precision Data for Nitrogen using a 2.0 mg N/L standard

**% RSD =0.85**

Standard Deviation (s) = 0.0174 mg N/L, Mean (x) = 1.05 mg N/L, Known Value = 2.00 mg N/L

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

Acq. Date: 20 Nov 2007



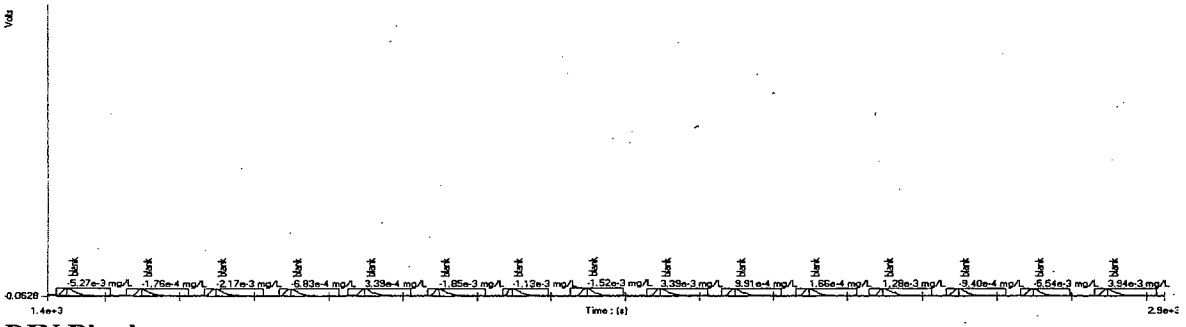

Carryover Study:

Two 20.0 mg N/L standards followed by three blanks

**Carryover Passed**

File Name: OM_11-26-2007_09-09-11AM.OMN

Acq. Date: 26 Nov 2007




## DIN Blanks

Average: -0.00061 mg N/L, SD = 0.0026 mg N/L. Calculated DIN Limits: Detection Limit = 0.0078 mg N/L, Decision Limit = 0.0157 mg N/L, Determination Limit = 0.0235 mg N/L.

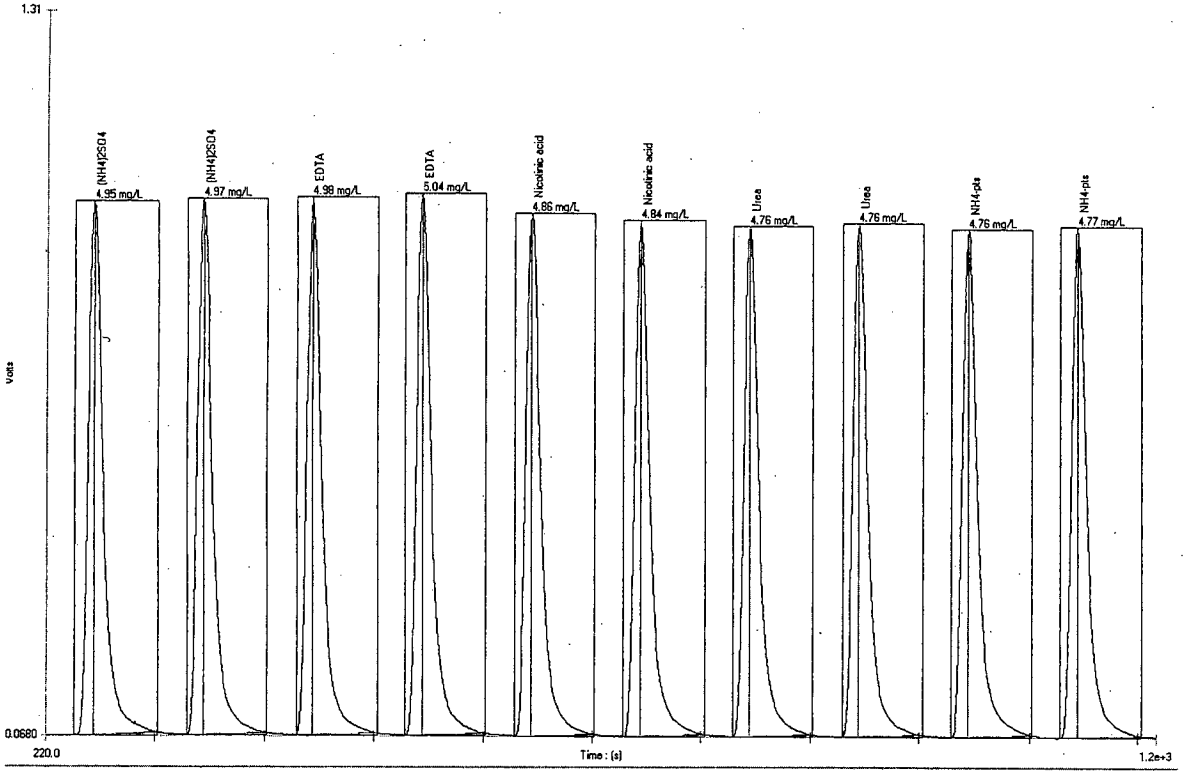
File Name: OM_11-20-2007_07-25-01AM.OMN

Acq. Date: 20 Nov 2007

Digestion Efficiency for Nitrogen containing compounds in DI water at 5.0 mg N/L

| Nitrogen Form | Mean Result (mg N/L) | %Recovery |
|---|---|---|
| Ammonia | 4.96 | 99.2 |
| EDTA | 5.01 | 100.2 |
| Nicotinic Acid | 4.85 | 97.0 |
| Urea | 4.76 | 95.2 |
| NPTS* | 4.77 | 95.3 |

* Ammonium p-toluenesulfonate




File Name: OM_11-26-2007_10-41-56AM.OMN
Acq. Date: 26 Nov 2007

**Spike recovery of Total Nitrogen in Wastewater**

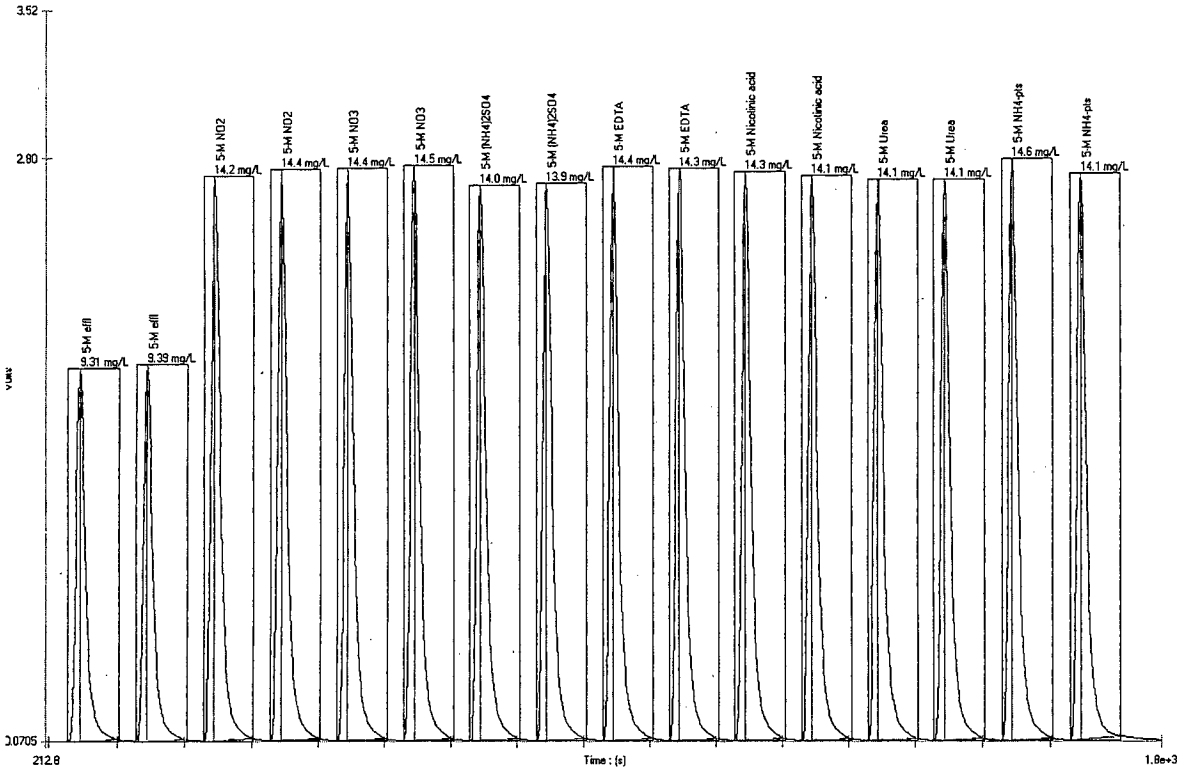
Initial total nitrogen concentration of wastewater was 9.35 mg N/L

Spiking level is 5.0 mg/L of each of the nitrogen compounds listed below:

| Nitrogen Compound | Spiked (mg N/L) | Spike Recovery |
|---|---|---|
| Nitrite | 14.30 | 99.0% |
| Nitrate | 14.45 | 102.0% |
| Ammonia | 13.95 | 92.0% |
| EDTA | 14.35 | 100.0% |
| Nicotinic Acid | 14.20 | 97.0% |
| Urea | 14.10 | 95.0% |
| NPTS* | 14.35 | 100.0% |

* Ammonium p-toluenesulfonate

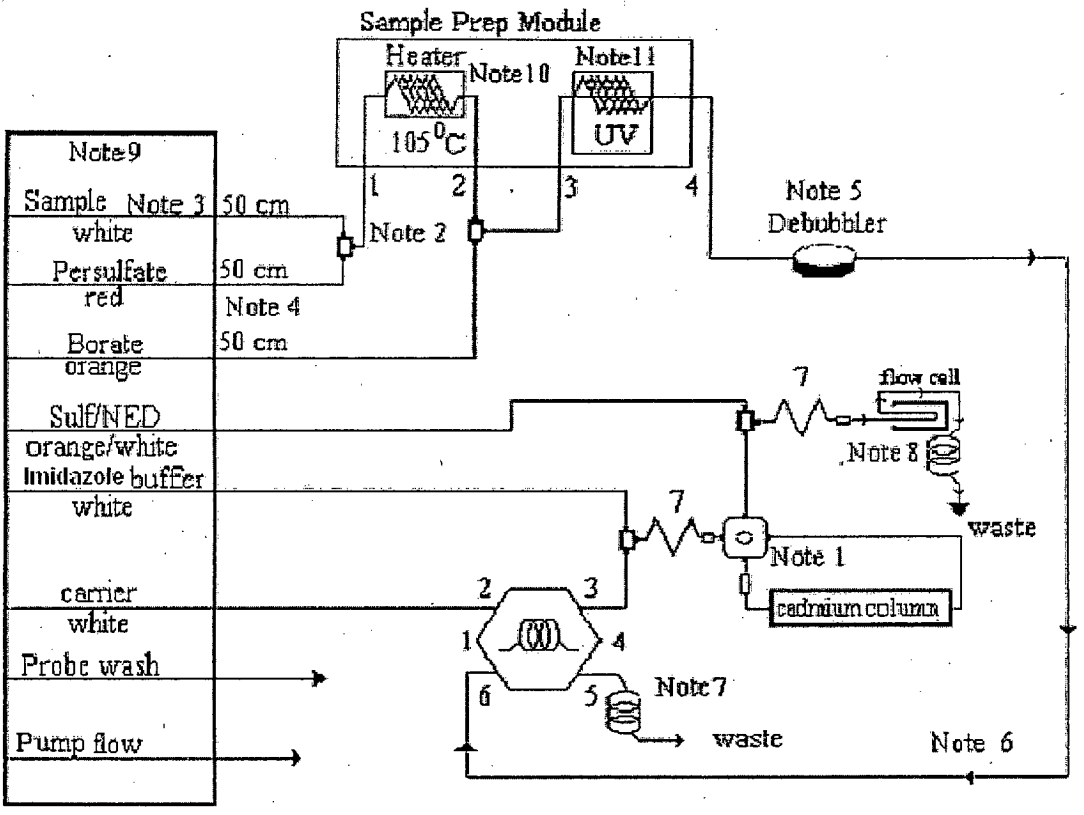
**Conclusion**: Spike recoveries of 92-102% were obtained using this method.




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

Acq. Date: 26 Nov 2007

## 17.3. TOTAL NITROGEN MANIFOLD DIAGRAM




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

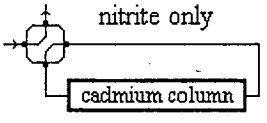
---

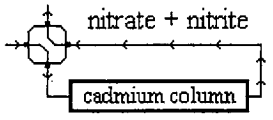
**Apparatus:** An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows 1200 cm of tubing wrapped around the heater block at the specified temperature.

**7:** **135** cm of tubing on a 7 cm coil support

---

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




**Note 2:** Tee's **'1'**and **'2'** are mounted on left side of manifold board.
**Note 3:** **From sampler to tee fitting '1':** The **white pump tube** is cut 2 cm outside of the tabs on both sides. The outlet of the sample pump tube is connected to tee fitting '1' with **50** cm of 0.8 mm id manifold tubing.

**Note 4:** **Persulfate (red) and borate (orange) pump tubes** are connected to tees **'1'** and **'2'** with **50** cm lengths of 0.8 mm id manifold tubing.

**Note 5:** **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. Please note that condensation may form at the outlet of this debubbler. A truly failed membrane will leak around the edge of the disc, not only through these ports.

**Note 6:** If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of the debubbler connected to Port 6 of the valve.

**Note 7:** The **100 cm back pressure loop** is 0.5 mm (0.022in.) i.d. tubing.

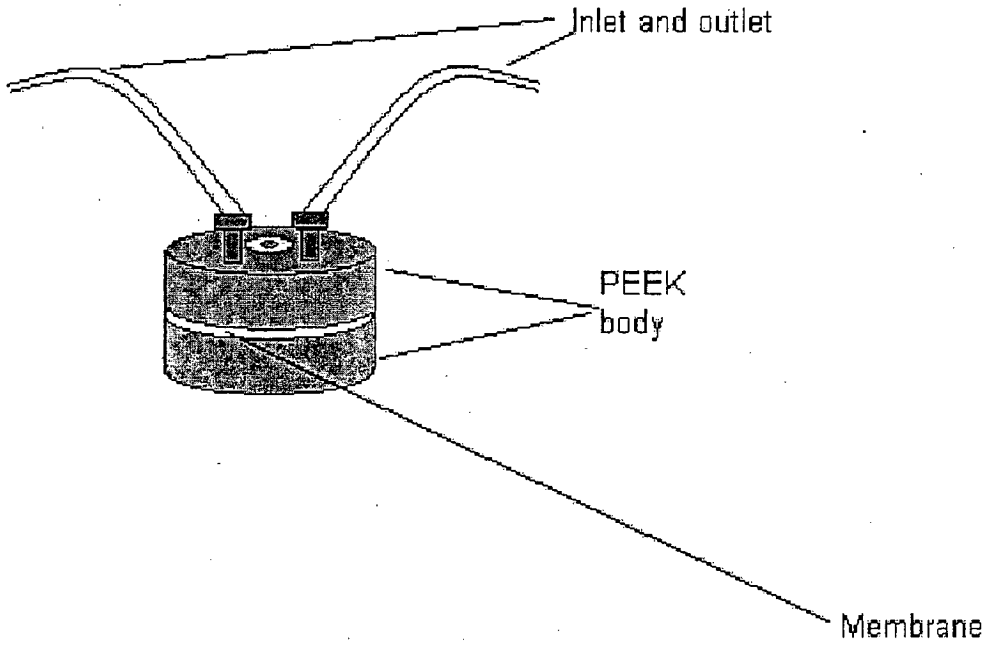
**Note 8:** The **200 cm back pressure loop** is 0.5 mm (0.022 in) i.d. tubing.

**Note 9:** **PVC PUMP TUBES MUST BE USED FOR THIS METHOD.**

**Note 10:** Heater (inside of the sample prep module): 1200 cm of 0.032" i.s. manifold tubing tubing is wrapped on a high temperature heater with **90 cm** remaining for connection at the inlet and outlet. (1380 cm total length) The outlet of tee **'1'** is connected to the heater inlet, and the heater outlet is connect to the inlet of tee **'2'**. Tee's **'1'** and **'2'** are mounted on the chemistry manifold board.

**Note 11:** The **UV-254 lamp (inside of the sample prep module) has 550 cm** of zeus tubing wrapped around the UV lamp with about **50 cm** of tubing remaining at each end for connections. (650 cm total length) The outlet of tee **'2'** is connected to the UV inlet, and the UV outlet is connected to the tubular membrane debubbler.

## 17.4. DEBUBBLER:




This debubbler has holes in the bottom, and a circular membrane sandwiched between two round pices of tan PEEK. Typically, it does not require a backpressure loop on the outlet.

→ When a liquid other than water is passed through this debubbling unit, it is very important that DI water be pumped through it for 5-10 minutes, followed by pumping air for another 5-10 minutes at the end of each days run. This aids in removing salts, acids, and bases that could reduce the lifetime of the membrane, and at least partially dries the hydrophobic membrane material. Membranes typically last 1-3 weeks, or even longer with fastidious care.

**If the solution passing through the unit is very hot, it is not unusual to see water droplets on the outside. If bubbles are still entering in the fluid stream but not exiting at the outlet, the unit is still properly functioning despite this condensation.**

Membranes are replaced by removal of the Allen screw in the center of the block. The "expired" membrane is removed, and a replacement centered. If the replacement membrane has any text on it, the membrane should be placed so that the text side faces the bottom of the unit.
The part numbers for this are as follows:

***85362 BUBBLE TRAP, QC8000/8500 (Not salable)***
***85363 BUBBLE TRAP, SPARE MEMBRANES, PK 5***
***85364 TUBING SET, BUBBLE TRAP QC8000/QC8500***
***85361 KIT, BUBBLE TRAP, QC8000/QC8500***

## 17.5. MEASURING NITRATE/NITRITE UTILIZING TN MANIFOLD

### 17.5.1. DATA SYSTEM PARAMETERS FOR NITRATE/NITRITE

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

**Low Range**

| | |
|---|---|
| Sample throughput: | 60 samples/h, 60 s/sample |
| Pump Speed: | 35 |
| Cycle Period: | 60 |

**Analyte Data:**

| | |
|---|---|
| Concentration Units: | mg N/L |
| Peak Base Width: | 67.6 s |
| Inject to Peak Start: | 28.9 s |
| Chemistry: | Direct/Bipolar |

**Calibration Data:**

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Concentration mg N/L | 2.00 | 1.00 | 0.40 | 0.20 | 0.10 | 0.04 | 0.02 | 0.01 | 0.00 |

| | |
|---|---|
| Calibration Fit Type: | 2nd Order Polynomial |
| Weighting Method: | 1/x |
| Force through zero: | No |

**Sampler Timing:**

| | |
|---|---|
| Min. Probe in Wash Period: | 15 s |
| Sample Period: | 20 s |

**Valve Timing:**

| | |
|---|---|
| Load Period: | 15 s |
| Inject Period: | 45 s |

## High Range

Sample throughput: 45 samples/h, 80 s/sample
Pump Speed: 35
Cycle Period: 80

**Analyte Data:**

Concentration Units: mg N/L
Peak Base Width: 67.6 s
Inject to Peak Start: 28.9 s
Chemistry: Direct/Bipolar

**Calibration Data:**

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Concentration mg N/L | 20.0 | 10.0 | 5.00 | 2.00 | 1.00 | 0.40 | 0.20 | 0.10 | 0.00 |

Calibration Fit Type: 2nd Order Polynomial
Weighting Method: 1/x
Force through zero: No

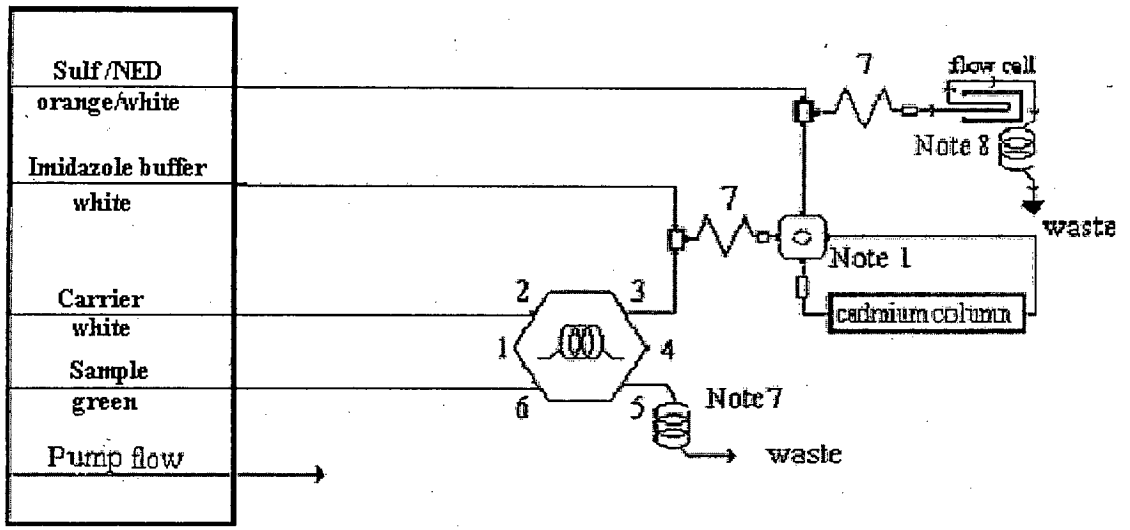
**Sampler Timing:**

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

**Valve Timing:**

Load Period: 10 s
Inject Period: 70 s

## Nitrate manifold




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

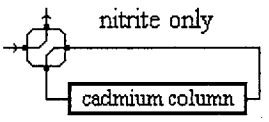
---

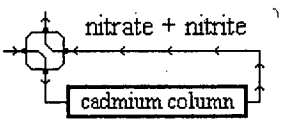
**Apparatus:** An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required.

**7:** **135** cm of tubing on a 7 cm coil support

---

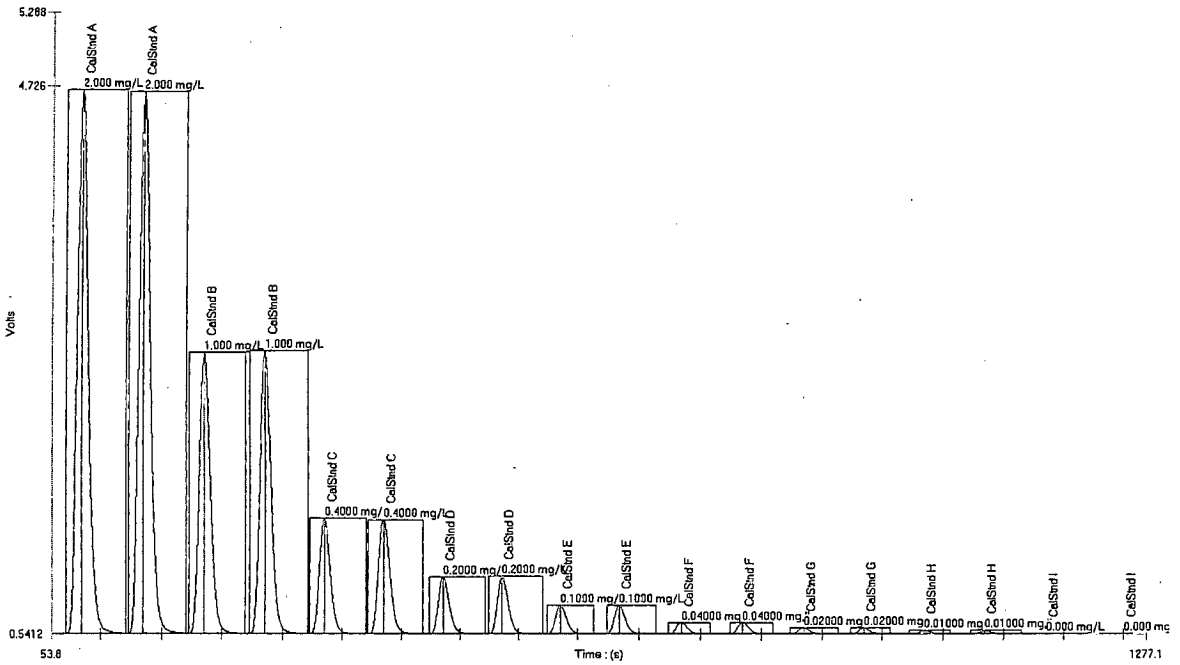
**Note 1:** This is a two state valve used to place the cadmium column in-line with the manifold.




When changing the in-line manifold over to run for non-digested nitrate/nitrite, you can remove the debubbler from port 6 of the injection valve to speed up the time to valve time.

## Calibration Data for Nitrate/Nitrite Low Range



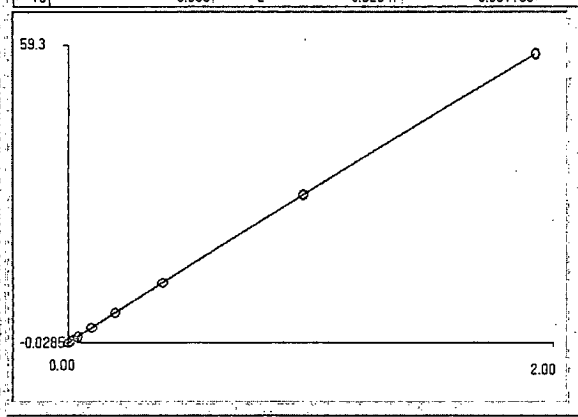

File Name: 12-2 cal support
Acq. Date: 2 Dec 2010

## Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

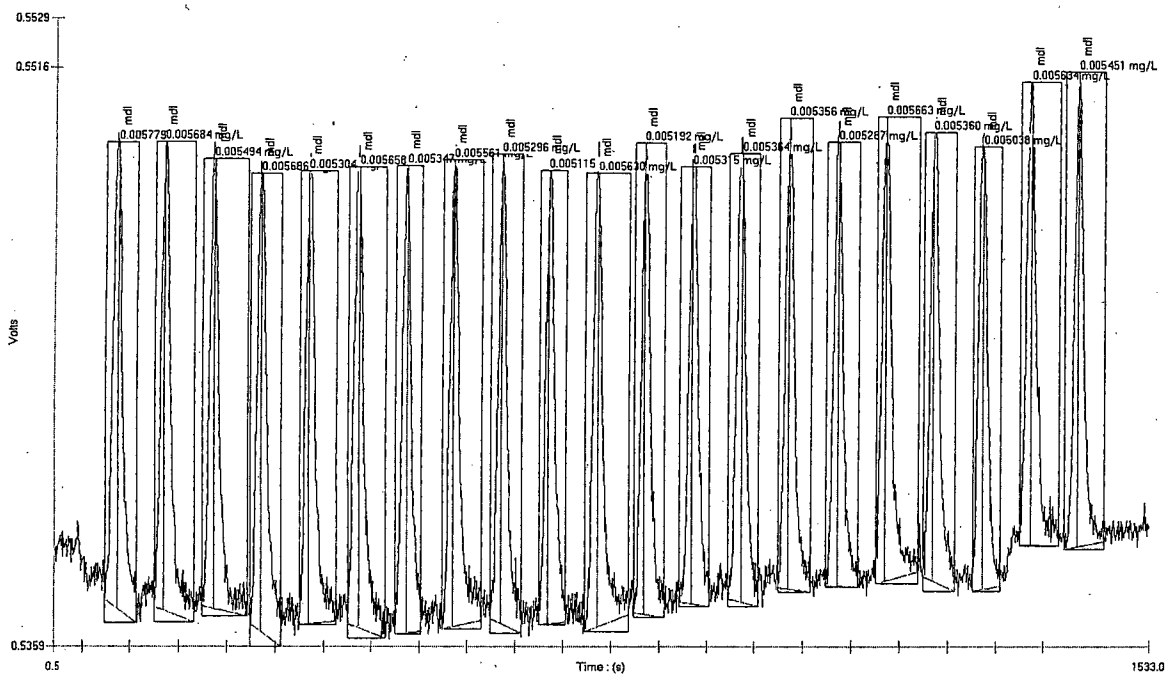
| | Known Conc. (mg/L) | Rep. | Peak Area (V.s) | Peak Height (V) | % RSD | % Resid. | Unused | Det. Conc (mg/L) | Date | Time |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 2.000 | 1 | 59.26 | 4.156 | 0.3 | -0.2 | ☐ | 2.003 | 12/2/2010 | 12:01:09 PM |
| 2 | 2.000 | 2 | 59.04 | 4.141 | 0.3 | 0.2 | ☐ | 1.995 | 12/2/2010 | 12:02:17 PM |
| 3 | 1.000 | 1 | 30.31 | 2.151 | 0.4 | 0.1 | ☐ | 0.9992 | 12/2/2010 | 12:03:24 PM |
| 4 | 1.000 | 2 | 30.47 | 2.162 | 0.4 | -0.4 | ☐ | 1.004 | 12/2/2010 | 12:04:32 PM |
| 5 | 0.4000 | 1 | 12.34 | 0.8835 | 0.1 | 0.0 | ☐ | 0.3999 | 12/2/2010 | 12:05:39 PM |
| 6 | 0.4000 | 2 | 12.32 | 0.8753 | 0.1 | 0.2 | ☐ | 0.3991 | 12/2/2010 | 12:06:46 PM |
| 7 | 0.2000 | 1 | 6.165 | 0.4392 | 0.4 | 0.7 | ☐ | 0.1983 | 12/2/2010 | 12:07:53 PM |
| 8 | 0.2000 | 2 | 6.199 | 0.4414 | 0.4 | 0.2 | ☐ | 0.1994 | 12/2/2010 | 12:09:00 PM |
| 9 | 0.1000 | 1 | 3.110 | 0.2218 | 0.1 | 0.4 | ☐ | 0.09944 | 12/2/2010 | 12:10:05 PM |
| 10 | 0.1000 | 2 | 3.107 | 0.2211 | 0.1 | 0.6 | ☐ | 0.09934 | 12/2/2010 | 12:11:11 PM |
| 11 | 0.04000 | 1 | 1.254 | 0.08881 | 0.5 | 0.9 | ☐ | 0.03960 | 12/2/2010 | 12:12:20 PM |
| 12 | 0.04000 | 2 | 1.245 | 0.08799 | 0.5 | 1.6 | ☐ | 0.03931 | 12/2/2010 | 12:13:29 PM |
| 13 | 0.02000 | 1 | 0.6658 | 0.04667 | 0.2 | -3.3 | ☐ | 0.02067 | 12/2/2010 | 12:14:37 PM |
| 14 | 0.02000 | 2 | 0.6635 | 0.04636 | 0.2 | -2.9 | ☐ | 0.02060 | 12/2/2010 | 12:15:45 PM |
| 15 | 0.01000 | 1 | 0.3566 | 0.02529 | 0.6 | -6.8 | ☐ | 0.01073 | 12/2/2010 | 12:16:53 PM |
| 16 | 0.01000 | 2 | 0.3598 | 0.02513 | 0.6 | -7.7 | ☐ | 0.01084 | 12/2/2010 | 12:18:01 PM |
| 17 | 0.000 | 1 | -0.02853 | -7.687e-4 | | | ☐ | -0.001637 | 12/2/2010 | 12:19:08 PM |
| 18 | 0.000 | 2 | 0.02047 | 0.001100 | | | ☐ | -6.376e-5 | 12/2/2010 | 12:20:16 PM |




Conc = 2.876e-5 * Area^2 + 0.03211 * Area - 7.210e-4
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



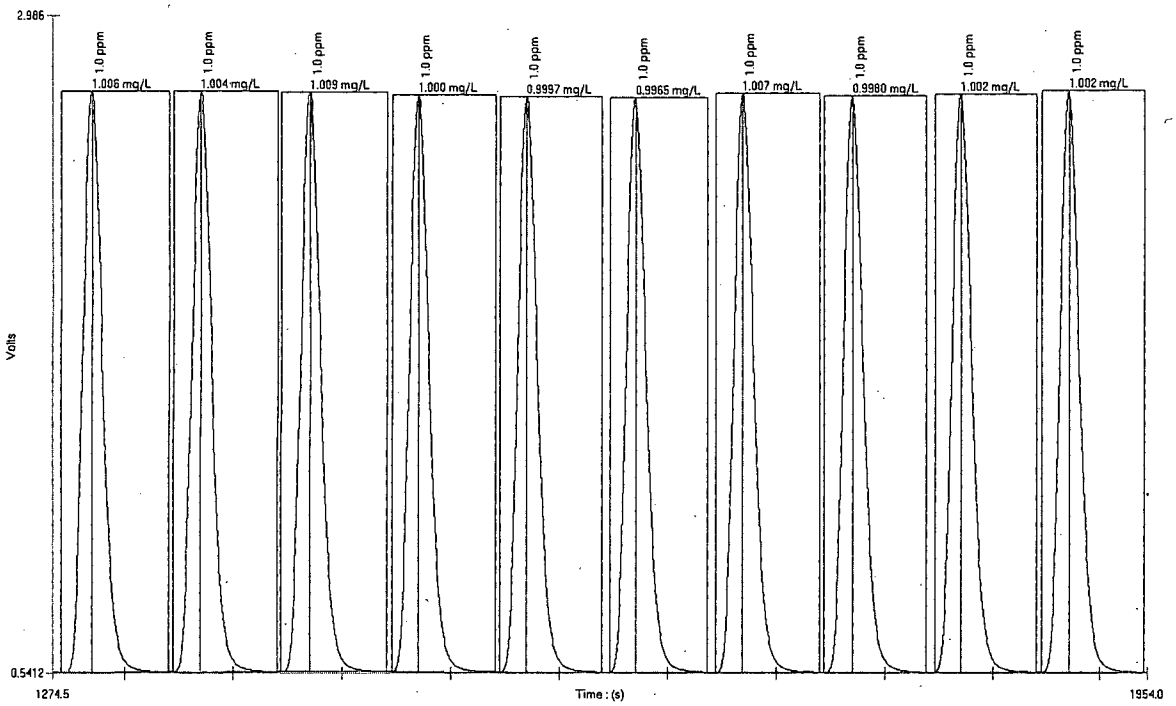

Method Detection Limit for Nitrate/Nitrite using a 0.005 mg N/L standard

**MDL= 0.0005 mg N/L**

Standard Deviation (s) = 0.0002 mg N/L, Mean (x) = 0.054 mg N/L, Known Value = 0.005 mg N/L

File Name: 12-2 mdl 21

Acq. Date: 2 Dec 2010



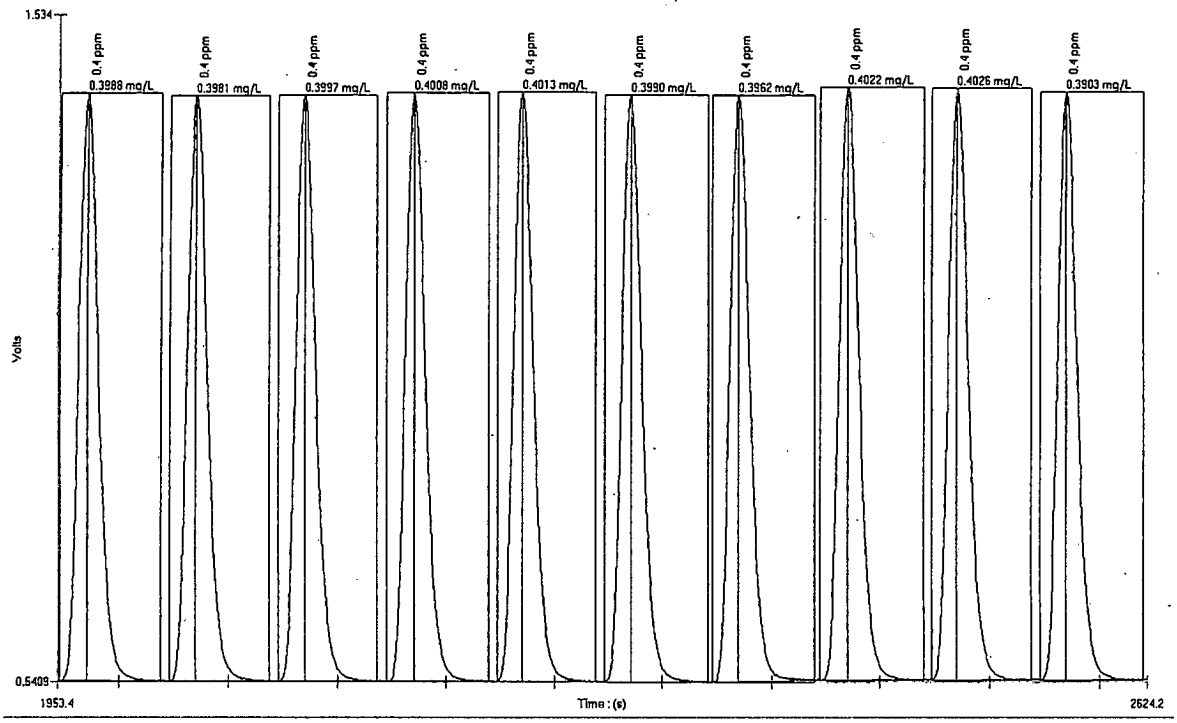

Precision Data for Nitrate/Nitrite using a 1.0 mg N/L standard

**% RSD = 0.40**

Standard Deviation (s) = 0.004 mg N/L, Mean (x) = 1.00 mg N/L, Known Value = 1.00 mg N/L

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010



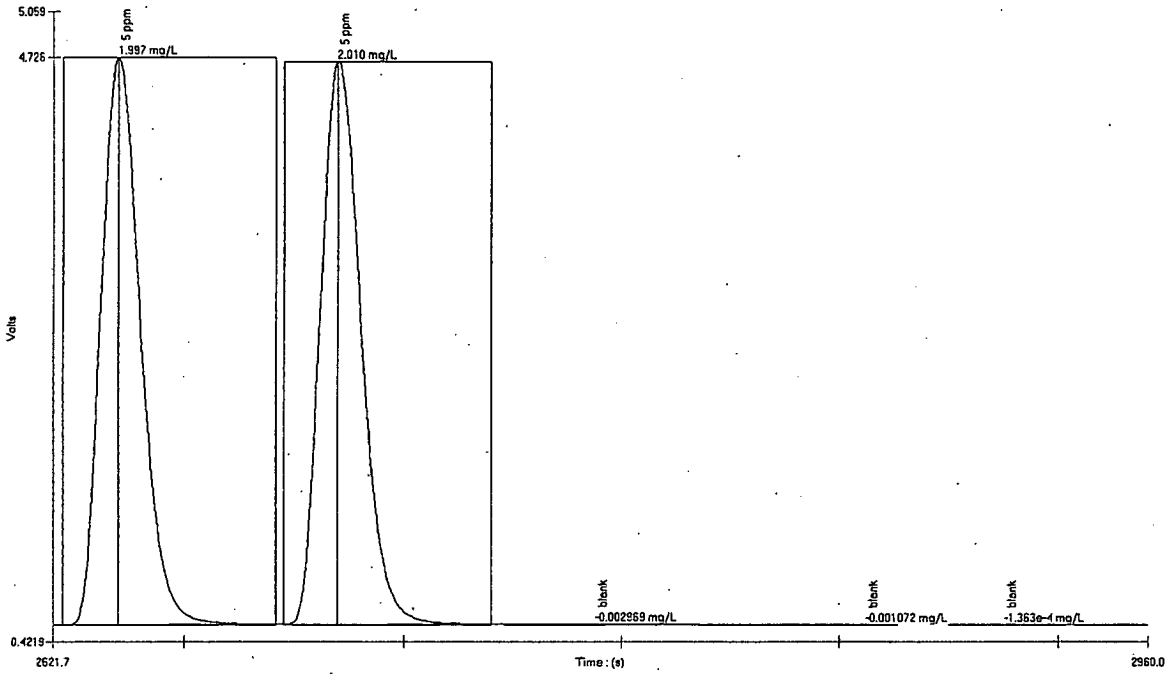

Precision Data for Nitrate/Nitrite using a 0.4 mg N/L standard

**% RSD = 0.90**

Standard Deviation (s) = 0.0036 mg N/L, Mean (x) = 0.40 mg N/L, Known Value = 0.40 mg N/L

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010




Carryover Study:

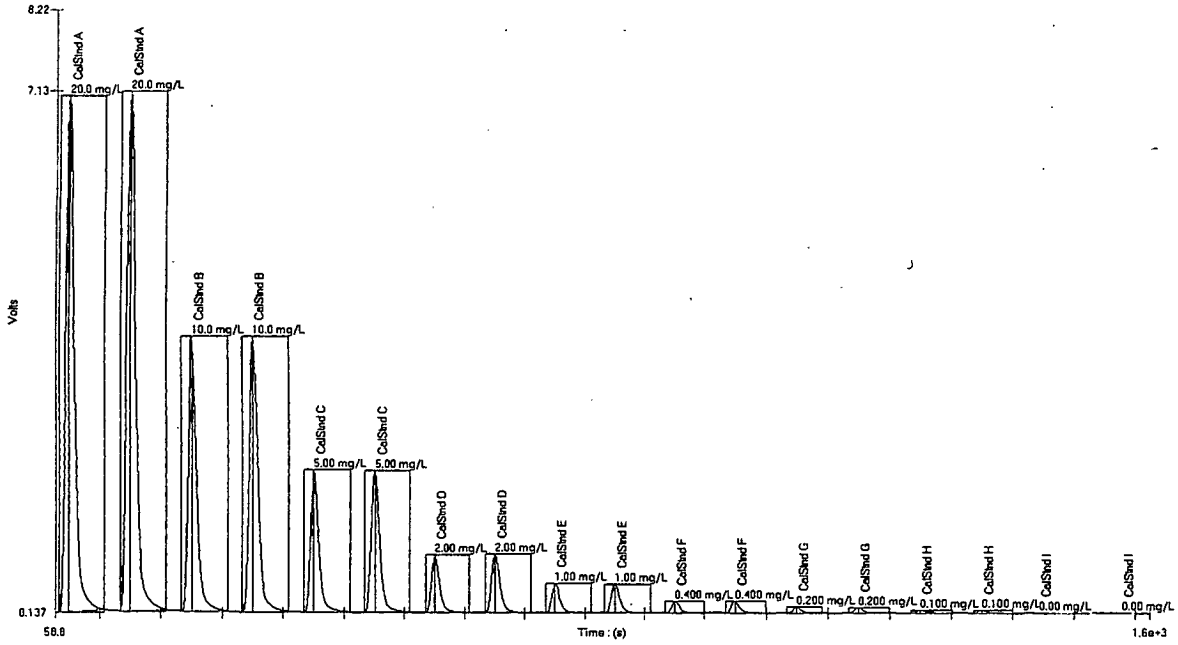
Two 2.0 mg N/L standards followed by three blanks

**Carryover Passed**

File Name: 12-2 cal support

Acq. Date: 2 Dec 2010

## Calibration Data for Nitrate/Nitrite High Range



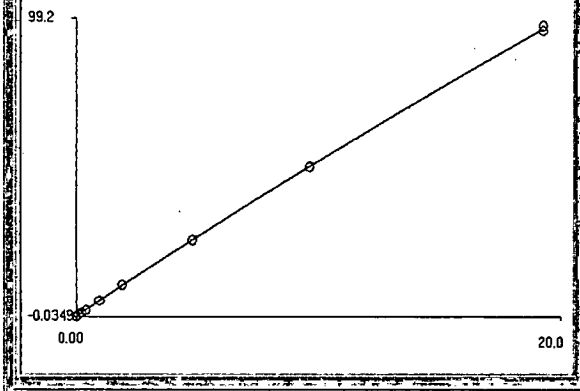

File Name: 11-12 cal HR.omn
Acq. Date: 12 Nov 2009

## Calibration Graph and Statistics

Calibration Results - Channel 2

NO3

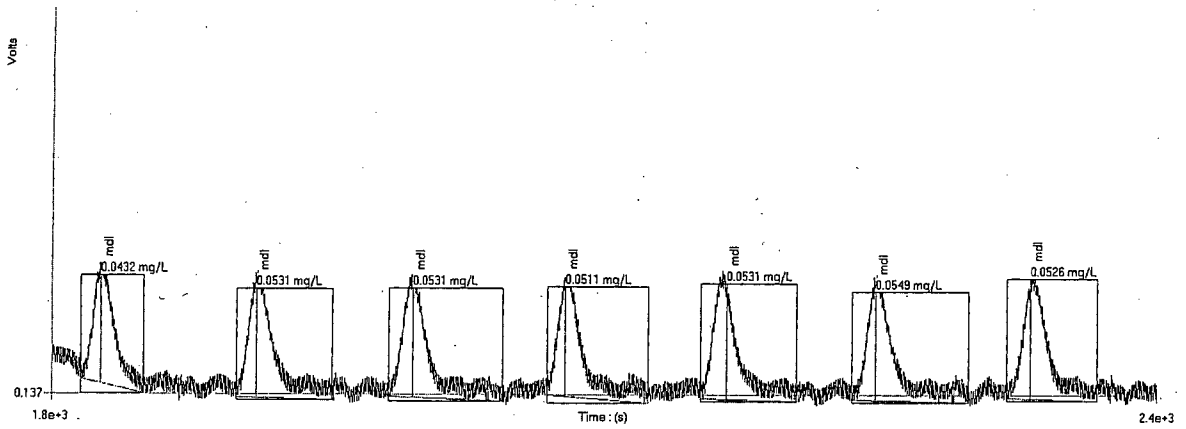
| | Known Conc. (mg/L) | Rep. | Peak Area (V.s) | Peak Height (V) | % RSD | % Resid. | Unused | Det. Conc (mg/L) | Date | Time |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 20.0 | 1 | 97.5 | 6.92 | 1.2 | 0.7 | ☐ | 19.8 | 11/12/2009 | 7:55:43 AM |
| 2 | 20.0 | 2 | 99.2 | 6.97 | 1.2 | -1.0 | ☐ | 20.2 | 11/12/2009 | 7:57:10 AM |
| 3 | 10.0 | 1 | 51.0 | 3.70 | 0.4 | 0.7 | ☐ | 9.95 | 11/12/2009 | 7:58:39 AM |
| 4 | 10.0 | 2 | 51.3 | 3.70 | 0.4 | 0.1 | ☐ | 10.0 | 11/12/2009 | 8:00:06 AM |
| 5 | 5.00 | 1 | 26.2 | 1.91 | 0.3 | 0.2 | ☐ | 4.99 | 11/12/2009 | 8:01:34 AM |
| 6 | 5.00 | 2 | 26.1 | 1.90 | 0.3 | 0.6 | ☐ | 4.97 | 11/12/2009 | 8:03:01 AM |
| 7 | 2.00 | 1 | 10.7 | 0.778 | 1.0 | -0.2 | ☐ | 2.00 | 11/12/2009 | 8:04:29 AM |
| 8 | 2.00 | 2 | 10.8 | 0.784 | 1.0 | -1.7 | ☐ | 2.03 | 11/12/2009 | 8:05:56 AM |
| 9 | 1.00 | 1 | 5.41 | 0.391 | 0.1 | -1.4 | ☐ | 1.01 | 11/12/2009 | 8:07:23 AM |
| 10 | 1.00 | 2 | 5.40 | 0.389 | 0.1 | -1.2 | ☐ | 1.01 | 11/12/2009 | 8:08:49 AM |
| 11 | 0.400 | 1 | 2.16 | 0.155 | 0.8 | -0.6 | ☐ | 0.401 | 11/12/2009 | 8:10:15 AM |
| 12 | 0.400 | 2 | 2.16 | 0.157 | 0.8 | -1.7 | ☐ | 0.406 | 11/12/2009 | 8:11:42 AM |
| 13 | 0.200 | 1 | 1.06 | 0.0779 | 1.2 | 1.5 | ☐ | 0.197 | 11/12/2009 | 8:13:10 AM |
| 14 | 0.200 | 2 | 1.08 | 0.0759 | 1.2 | -0.2 | ☐ | 0.200 | 11/12/2009 | 8:14:39 AM |
| 15 | 0.100 | 1 | 0.548 | 0.0389 | 1.7 | -0.9 | ☐ | 0.101 | 11/12/2009 | 8:16:08 AM |
| 16 | 0.100 | 2 | 0.561 | 0.0386 | 1.7 | -3.4 | ☐ | 0.104 | 11/12/2009 | 8:17:36 AM |
| 17 | 0.00 | 1 | 5.10e-3 | 3.15e-3 | | | ☐ | 3.91e-5 | 11/12/2009 | 8:19:05 AM |
| 18 | 0.00 | 2 | -0.0349 | 2.07e-3 | | | ☐ | -7.41e-3 | 11/12/2009 | 8:20:33 AM |




Area = -0.0221 * Conc^2 + 5.35 * Conc + 7.75e-3
Conc = 1.77e-4 * Area^2 + 0.186 * Area - 9.09e-4
Correlation Coefficient (r) = 1.00000

Weighting : 1/x

Settings



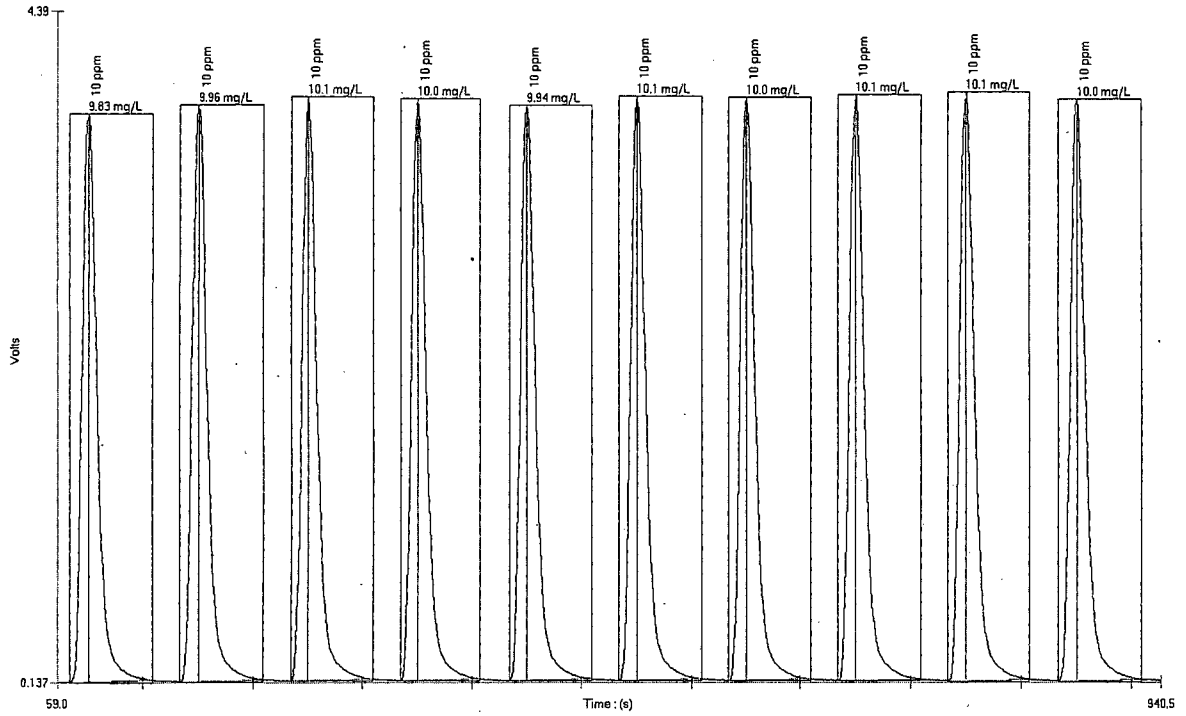

Method Detection Limit for Nitrate/Nitrite using a 0.05 mg N/L standard

**MDL= 0.012 mg N/L**

Standard Deviation (s) = 0.004 mg N/L, Mean (x) = 0.052 mg N/L, Known Value = 0.05 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009



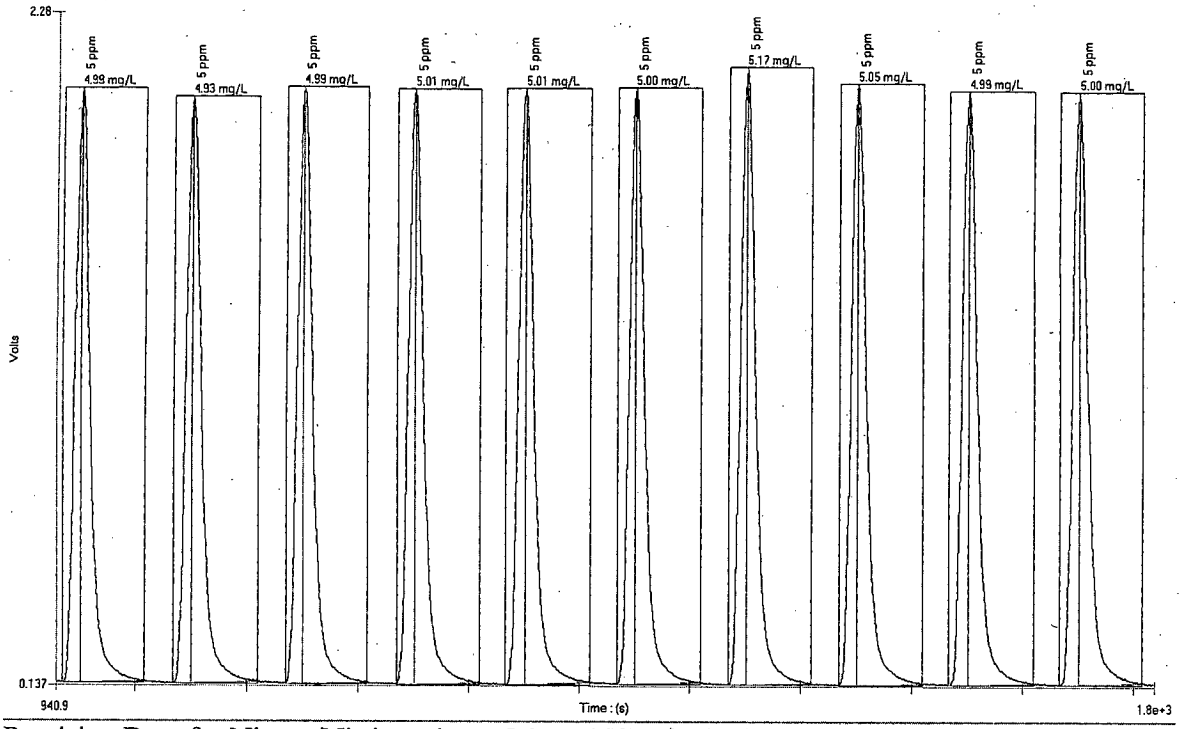

Precision Data for Nitrate/Nitrite using a 10.0 mg N/L standard

**% RSD =0.90**

Standard Deviation (s) = 0.09 mg N/L, Mean (x) = 10.01 mg N/L, Known Value = 10.0 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009



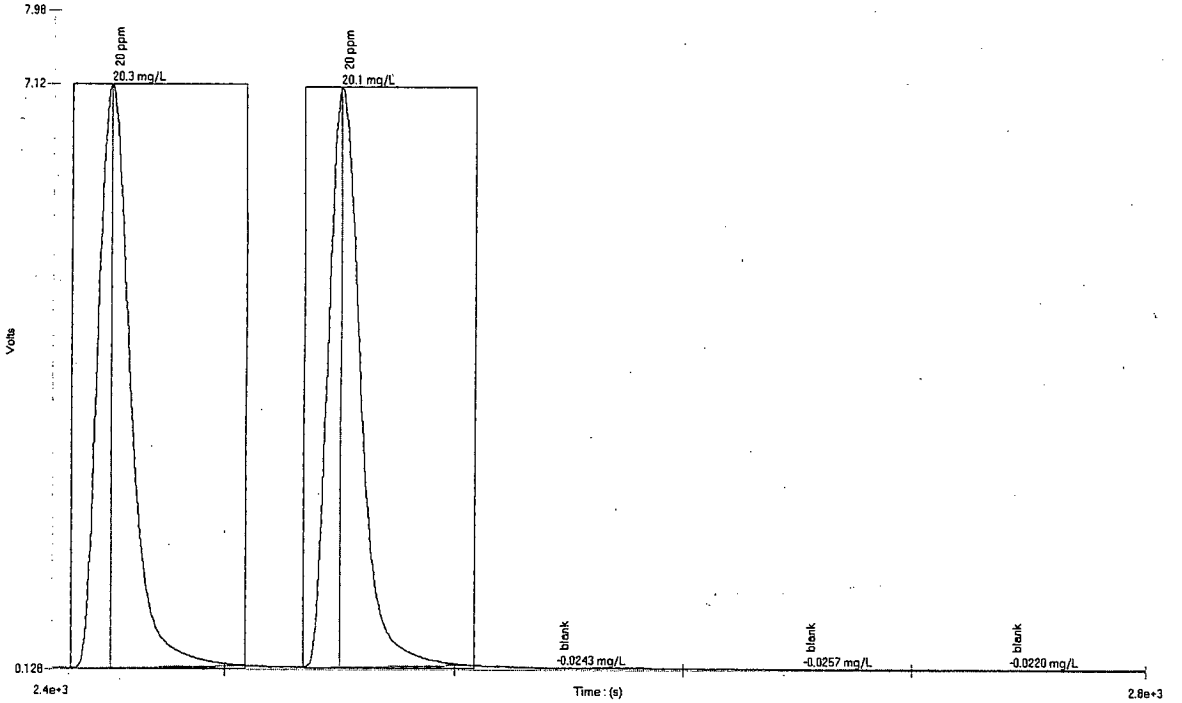

## Precision Data for Nitrate/Nitrite using a 5.0 mg N/L standard

**% RSD =1.24**

Standard Deviation (s) = 0.062 mg N/L, Mean (x) = 5.01 mg N/L, Known Value = 5.00 mg N/L

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009




## Carryover Study:

Two 20.0 mg N/L standards followed by three blanks

**Carryover Passed**

File Name: 11-12 support HR.omn

Acq. Date: 12 Nov 2009

# QuikChem® Method 10-115-01-3-E

# DETERMINATION OF TOTAL PHOSPHORUS BY FLOW INJECTION ANALYSIS COLORIMETRY (IN-LINE PERSULFATE DIGESTION METHOD)

**(Method also includes Manifold Alterations to Analyze Ortho Phosphate)**

**Written by Lynn Egan**

**Applications Group**

**Revision Date:**

**3 December 2010**

**LACHAT INSTRUMENTS**
**5600 LINDBURGH DRIVE**
**LOVELAND, CO 80539 USA**

LACHAT INSTRUMENTS
A Hach Company Brand

## QuikChem® Method 10-115-01-3-E

# Total Phosphorous (In-Line Persulfate Digestion)

### 10 to 500 µg P/L

## – Principle –

The method is based on the digestion of various phosphorous forms and conversion to phosphate by peroxodisulfate with an in-line UV digestion. Organic phosphorus is converted to orthophosphate by UV catalyzed persulfate digestion. Polyphosphates are converted to orthophosphate by sulfuric acid digestion. The digestion process occurs prior to the sample valve. A portion of the digested sample is then injected and phosphate is determined by FIA.

Wastewater samples are acid preserved and filtered. When this is the case, in-line digestion results match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

After digestion the orthophosphate ion ($PO_4^{3-}$) reacts with ammonium molybdate and antimony potassium tartrate to form a phosphomolybdate complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

## -Interferences-

1. Silicate is not a significant interference when using this method. 1000 mg/L $SiO_2$ gives a response of approximately 6 µg P/L.
2. Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

## – Special Apparatus –

Please see Parts and Price list for Ordering Information

1. Lachat sample preparation module, A30**X**03 **X** =1 for 110V, **X**=2 for 220V) with UV-254 nm lamp.
2. Heater
3. PVC PUMP TUBES MUST BE USED FOR THIS METHOD.
4. Glass standard and sample vials must be used for this method.

Revised by S. Tucker 3 December 2010. Written and copyrighted © by Lynn Egan on 02 May 2002 by **Lachat Instruments, 5600 Lindburgh Drive, Loveland, CO 80539 USA**. Phone: 970-663-1377 FAX: 970-962-6710.

# CONTENTS

# QuikChem® Method 10-115-01-3-E

# DETERMINATION OF TOTAL PHOSPHORUS BY FIA COLORIMETRY WITH ON-LINE DIGESTION

## 1. SCOPE AND APPLICATION

1.1. This method covers the determination of total phosphorus in drinking, ground, and surface waters, and domestic and industrial wastes. Wastewater samples are acid preserved and filtered. When this is the case, in-line digestion results match the manual off-line digestion. If samples are not filtered, in-line results will be 1-15% low compared with off-line digestion. Surface water samples may not require filtration but this should be verified with a sample containing high levels of solids.

1.2. The method of determination is based on reactions that are specific for the orthophosphate ($PO_4^{3-}$) ion.

1.3. The applicable range is 10 to 500 µg P/L. The statistically determined method detection limit is 1.4 µg P/L. The method throughput is 32 injections per hour.

## 2 SUMMARY OF METHOD

2.1 The method is based on the digestion of various phosphorous forms to phosphate by peroxodisulfate with an on-line UV digestion. Organic phosphorus is converted to orthophosphate by persulfate digestion catalyzed by UV light. Polyphosphates are converted to orthophosphate by sulfuric acid digestion. The digestion process occurs prior to the sample valve. A portion of the digested sample is then injected and or the phosphates determined by FIA.

2.2 The orthophosphate ion ($PO_4^{3-}$) reacts with ammonium molybdate and antimony potassium tartrate under acidic conditions to form a complex. This complex is reduced with ascorbic acid to form a blue complex which absorbs light at 880 nm. The absorbance is proportional to the concentration of orthophosphate in the sample.

## 3. DEFINITIONS

3.1. CALIBRATION BLANK (CB) -- A volume of reagent water in the same matrix as the calibration standards, but without the analyte.

3.2. CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3. INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.4. LABORATORY SPIKED BLANK (LSB) -- an aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory.

The LSB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.5. LABORATORY SPIKED SAMPLE MATRIX (LSM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LSM is analyzed exactly like sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.6. LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that is digested exactly as a sample including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.7. LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.8. MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.9. METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.10. PRACTICAL QUANTITION LIMIT (PQL) -- The lower level where measurements become quantitatively useful is called the PQL. The PQL is defined as PQL = 10∗s, where s = the standard deviation of 21 replicates of a standard 2.5 - 5 times the MDL.

3.11. QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to spike an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.12. STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

## 4. INTERFERENCES

4.1. Silicate is not a significant interference when using this method. 1000 mg/L SiO2 gives a response of approximately 6 µg P/L.

4.2. Glassware contamination is a problem in low level phosphorus determinations. Glassware should be washed with 1:1 HCl and rinsed with deionized water. Commercial detergents should rarely be needed but, if they are used, use special phosphate-free preparations for lab glassware.

## 5. SAFETY

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2. Each laboratory is responsible for maintaining a current awareness file of the Occupational Health and Safety Act (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3. The following chemicals have the potential to be highly toxic or hazardous, for detailed explanation consult the MSDS.

5.3.1. Sulfuric Acid

5.3.2. Sodium Dodecyl Sulfate (SDS)

5.3.3. Potassium persulfate

5.3.4. antimony potassium tartrate

## 6. EQUIPMENT AND SUPPLIES

6.1. Balance -- analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Glassware -- Class A volumetric flasks and pipettes or plastic containers as required. Samples may be stored in plastic or glass.

6.3. Flow injection analysis equipment designed to deliver and react sample and reagents in the required order and ratios.

6.3.1. Sampler

6.3.2. Multichannel proportioning pump

6.3.3. Reaction unit or manifold

6.3.4. Colorimetric detector

6.3.5. Data system

6.4. Special Apparatus

6.4.1. In-line TN/TP sample prep module with 254 nm lamp.

6.4.2. PVC PUMP TUBES MUST BE USED FOR THIS METHOD.

6.4.3. Glass standard and sample vials must be used with this method.

## 7. REAGENTS AND STANDARDS

### 7.1. PREPARATION OF REAGENTS

Use deionized water (10 megohm) for all solutions.

**Degassing with helium:**

To prevent bubble formation, degas all solutions except the standards with helium. Use He at 140kPa (20 $lb/in^2$) through a helium degassing tube (Lachat Part No. 50100.) Bubble He through the solution for one minute.

**Reagent 1. Stock Ammonium Molybdate Solution**

**By Volume:** In a **1 L** volumetric flask, **dissolve 40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24}{\cdot}4H_2O]$ in approximately **800 mL DI water**. Dilute to the mark and mix with a magnetic stirrer for at least four hours. The solution can be stored in plastic for up to two months if refrigerated.

**By Weight:** To a tared **1 L** container, add **40.0 g ammonium molybdate tetrahydrate** $[(NH_4)_6Mo_7O_{24}{\cdot}4H_2O]$ and **983 g DI water**. Mix with a magnetic stirrer for at least four hours. The solution can be stored in plastic for up to two months if refrigerated.

**Reagent 2. Stock Antimony Potassium Tartrate Solution**

**By Volume:** In a **1 L** volumetric flask, dissolve **3.22 g antimony potassium tartrate, potassium antimonyl tartrate trihydrate** $C_8H_4O_{12}K_2Sb_2{\cdot}3H_2O$) or **dissolve 3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$) in approximately **800 mL DI water**. Dilute to the mark and mix with a magnetic stirrer until dissolved. The solution can be stored in dark plastic for up to two months if refrigerated.

**By Weight:** To a **1 L** dark, tared container, **add 3.22 g antimony potassium tartrate, potassium antimonyl tartrate trihydrate** ($C_8H_4O_{12}K_2Sb_2{\cdot}3H_2O$) or **dissolve 3.0 g antimony potassium tartrate** (potassium antimonyl tartrate hemihydrate $K(SbO)C_4H_4O_6{\cdot}1/2H_2O$) and **995 g DI water**. Mix with a magnetic stirrer until dissolved. The solution can be stored in dark plastic for up to two months if refrigerated.

**Reagent 3. Molybdate Color Reagent**

**By Volume:** To a **1 L** volumetric flask, add about **500 mL DI water**, and then add **25 mL Sulfuric Acid** ($H_2SO_4$). Stir or swirl to mix. Then add **213 mL Ammonium Molybdate Solution** (Reagent 1) and **72 mL Antimony Potassium Tartrate Solution** (Reagent 2). Dilute to the mark and stir to mix. Degas with helium. Prepare weekly, or if blue color or yellow precipitate develops.

**By Weight:** To a tared **1 L** container, add **690g DI water**, and **47.8 g Sulfuric Acid** ($H_2SO_4$). Stir or swirl to mix. Then add **213 g Ammonium Molybdate Solution** (Reagent 1) and **72 Antimony Potassium Tartrate Solution** (Reagent 2). Stir to mix. Degas with helium. Prepare weekly or if blue color or yellow precipitate develops.

**Reagent 4. Ascorbic Acid Reducing Solution**

**By Volume:** In a **1 L** volumetric flask dissolve **70.0 g granular ascorbic acid** in about **700 mL DI water**. Dilute to the mark and mix with a magnetic stirrer. Degas this

solution with helium. Add **1.0 g SDS** (sodium dodecyl sulfate Aldrich catalog no. 86,201-0). Mix with a magnetic stirrer. Prepare fresh every two days.

**By Weight:** To a tared **1 L** container, add **70.0 g granular ascorbic acid** and **970 g DI water**. Mix with a magnetic stirrer until dissolved. Degas this solution with helium. **Add 1.0 g SDS** (sodium dodecyl sulfate, Aldrich catalog no. 86,201-0). Mix with a magnetic stirrer. Prepare fresh every two days.

**Reagent 5. Sulfuric Acid carrier solution (0.45M)**

**By Volume:** In a **1 L** volumetric flask, add **30 mL sulfuric acid** ($H_2SO_4$) in **about 600 mL DI water**. Add **9.0 g potassium chloride** (KCl). Dilute to the mark and stir to mix. Degas this solution with helium after the solution is cool. Prepare weekly.

**By Weight:** To a tared **1 L** container, add **55.2 g sulfuric acid** ($H_2SO_4$) into **970 g DI water**. **Add 9.0 g potassium chloride** (KCl). Stir to mix. Degas this solution with helium after the solution is cool. Prepare weekly.

## 7.2. PREPARATION OF DIGESTION REAGENTS

**Reagent 6. Digestion Reagent 1**

**By Volume:** To a **1 L** volumetric flask add **500 mL DI water** and then add **106.5 mL sulfuric acid** ($H_2SO_4$). CAUTION, this solution will become very hot! Dilute to the mark and stir to mix. Allow to cool to room temperature prior to use. Prepare weekly.

**By Weight:** To a tared **1 L** container, add **893.5 g DI water** and then **add 196.0 g sulfuric acid** ($H_2SO_4$). CAUTION, this solution will become very hot ! Stir to mix. Allow to come to room temperature before use . Prepare weekly.

**Reagent 7. Digestion Reagent 2**

**By Volume:** To a **1 L** volumetric flask add **800 ml DI water** and then **add 26 g potassium persulfate** ($K_2S_2O_8$). Mix with a magnetic stirrer until dissolved. Dilute to the mark. Prepare weekly. Degas before using.

**By Weight:** To a tared **1 L** container, add **990 g DI water** and then **add 26 g potassium persulfate** ($K_2S_2O_8$). Mix with a magnetic stirrer until dissolved. Prepare weekly. Degas before using.

(Potassium persulfate from EM Science, catalog number PX1560-1, has been shown to give good results with this method.)

## 7.3. PREPARATION OF STANDARDS

**NOTE:** Standards are prepared in a matrix of 1.5 mL/L sulfuric acid. This is assumed to match the sulfuric acid added to the samples for preservation. If samples are not preserved, the matrix for the standards is DI water. If a different amount of acid is used for preservation, then standards should be prepared to match the acid level of the samples.

**Solution 1. 1.5 ml/L Sulfuric acid:**

**By Weight:** To a tared **4 L** container add **3994 g (mL) DI water** and then add **11.04 g (6 mL) sulfuric acid** ($H_2SO_4$) and mix.

**Standard 1. Stock Standard 250 mg P/L**

In a **1 L** volumetric flask **dissolve 1.099 g primary standard grade anhydrous potassium phosphate monobasic** ($KH_2PO_4$) that has been dried for one hour at 105°C in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare monthly.

**Standard 2. Intermediate Stock Standard 1.0 mg P/L**

**By Volume:** In a **1 L** volumetric flask, add about **550 mL solution 1**, and **4.0 mL Stock Standard** (Standard 1). Dilute to the mark with **solution 1**. Invert to mix. Prepare weekly.

**By Weight:** To a tared **1 L** container add about **4 g Stock Standard** (Standard 1). Divide the actual weight of the solution added by **0.004** and make up to this resulting total weight with **solution 1**. Shake to mix. Prepare weekly.

**Working Standards**

| **Working Standards** (Prepare Weekly) Concentration mg P/L | **A** 500 | **B** 250 | **C** 100 | **D** 50 | **E** 25 | **F** 10 | **G** 0 |
|---|---|---|---|---|---|---|---|
| **By Volume** | | | | | | | |
| Volume (mL) of **stock standard 2** diluted to 250 mL with **solution 1** | 125 | 62.5 | 25 | 12.5 | --- | --- | --- |
| Volume (mL) of **Standard D** diluted to 250mL with **Solution 1** | --- | --- | --- | --- | 125 | 50 | --- |
| **By Weight** | | | | | | | |
| Weight (g) of **stock standard 2** diluted to final weight (~250 g) divided by **factor** below with **solution 1** | 125 | 62.5 | 25 | 12.5 | --- | --- | --- |
| Weight (g) of **Standard D** diluted to ~250g with **Solution 1** | --- | --- | --- | | 125 | 50 | --- |
| **Division Factor** Divide exact weight of the standard by this **factor** to give final weight | 0.5 | 0.25 | 0.1 | 0.05 | 0.5 | 0.2 | --- |

## 7.4. PREPARATION OF DIGESTION CHECK STANDARDS

**Stock Standard 1. 1000 mg P/L, as phenyl phosphate (PP)**

**By Volume:** In a **1 L** volumetric flask, add **8.20 g phenyl phosphate** ($(C_6H_5OP(O)(ONa)_2\ 2H_2O$, FW = 254.09) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

**Stock Standard 2. 1000 mg P/L for trimethyl phosphate (TMP)**

**By Volume:** In a **1 L** volumetric flask, add **4.5 g trimethyl phosphate** ($(CH_3O)_3P(O)$, FW = 140.08) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

**Stock Standard 3. 1000 mg P/L for sodium pyrophosphate (2P)** ✓

**By Volume:** In a **1 L** volumetric flask, add **4.292 g sodium pyrophosphate** ($Na_4P_2O_7$ Fw = 265.90) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly. 2.146

**Stock Standard 4. 1000 mg P/L for sodium tripolyphosphate (3P)**

**By Volume:** In a **1 L** volumetric flask, add **4.66 g sodium tripolyphosphate 85%,** ($Na_5P_3O_{10}$ FW = 367.86) in about **800 mL DI water**. Dilute to the mark with **DI water** and invert to mix. Prepare fresh monthly.

**Working Stock Standard Solution 10.0 mg P/L**

**By Volume:** In a **1 L** volumetric flask, about **550 mL Solution 1** (1.5 mL $H_2SO_4$/L) and **10.0 mL Stock Standard 1, 2, 3, or 4**. Dilute to the mark with **Solution 1**. Invert to mix.

**By Weight:** To a tared **1 L** container, add about **10 g Stock Standard 1, 2, 3, or 4**. Divide the actual weight of the solution added by **0.01** and make up to this resulting total weight with **Solution 1** (1.5 mL $H_2SO_4$/L). Shake to mix.

| **Working Standard** | **A** |
|---|---|
| Concentration µg P/L | 500 |

**By Volume**

| | |
|---|---|
| Volume (mL) of **stock standards 1, 2, 3, or 4** diluted to **250 mL** with **Solution 1** | 12.5 |
| Volume (mL) of **Standard A** diluted to 250 mL with **Solution 1** | |

**By Weight**

| | |
|---|---|
| Weight (g) of **stock standards 1, 2, 3, or 4** diluted to final weight (~250 g) divided by **factor** below with **Solution 1** | 12.5 |
| Weight (g) of **Standard A** diluted to final weight (~250g) divided by **factor** below with **solution 1** | |
| **Division Factor**<br>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.

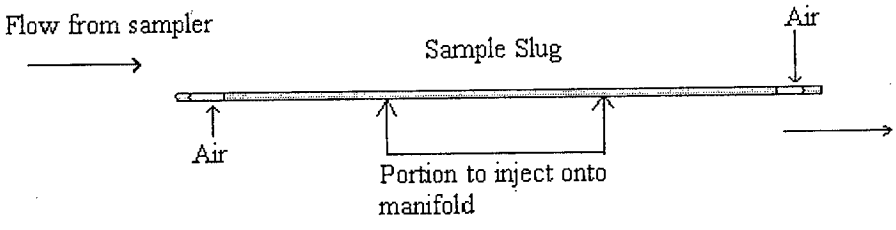
## 11.3 SYSTEM NOTES

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 |

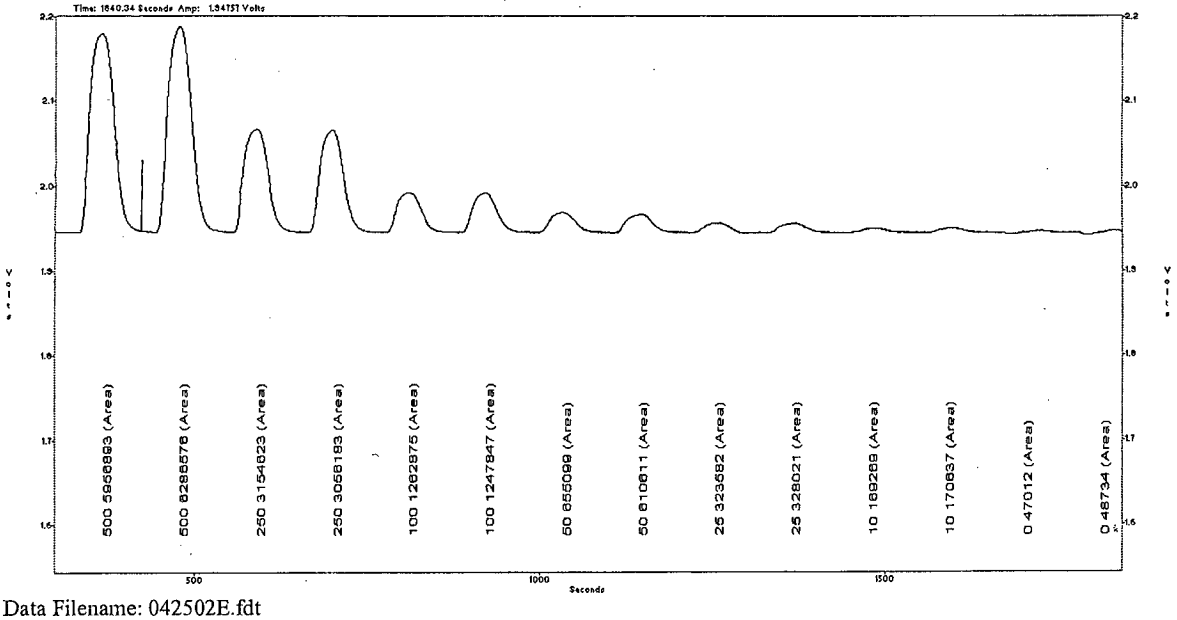
**Valve Timing:**

| | |
|---|---|
| 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

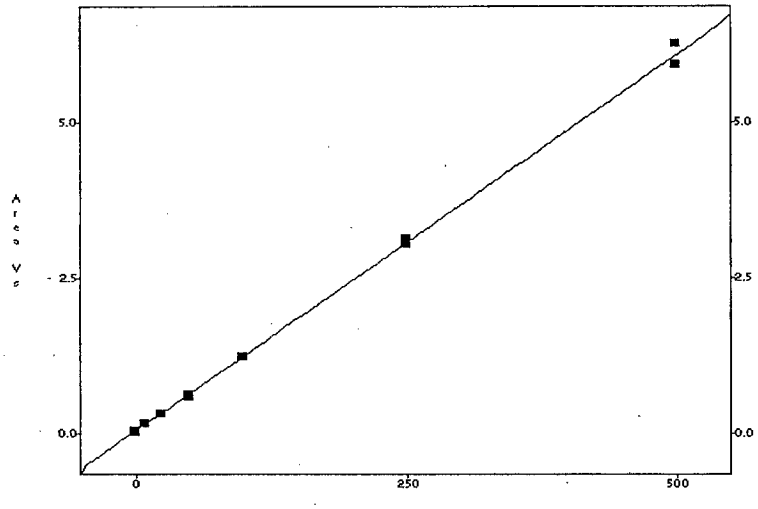
### Calibration Data for Total Phosphorus

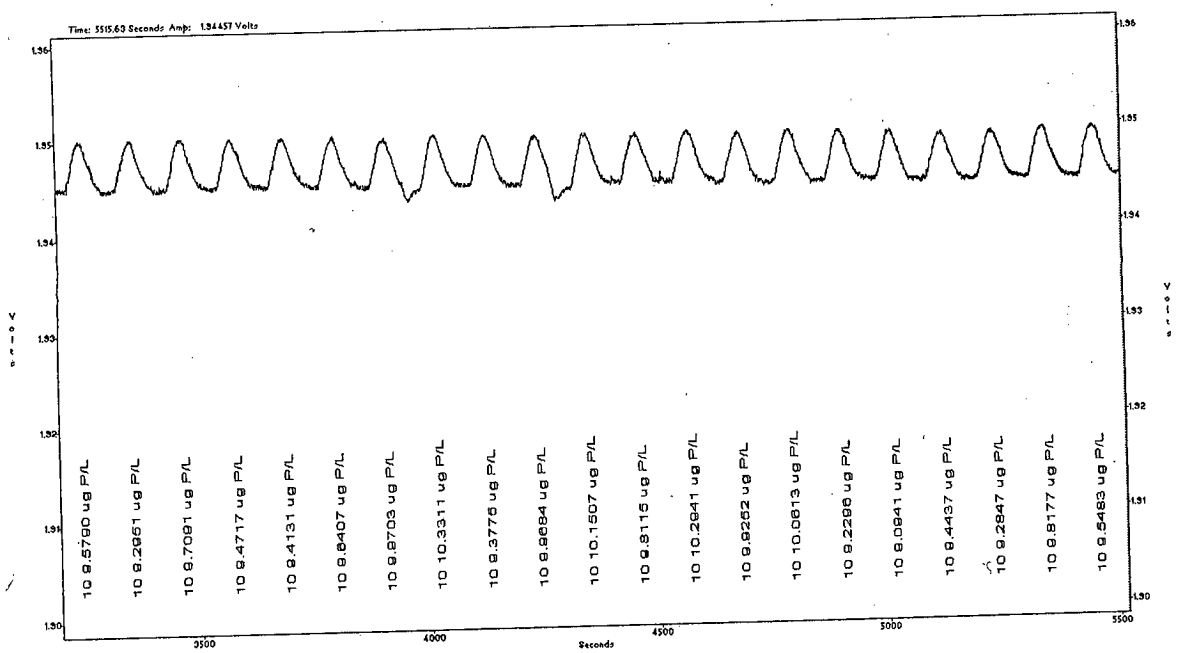



Data Filename: 042502E.fdt
Acq Date: 25 April 2002:

### 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 | *** |





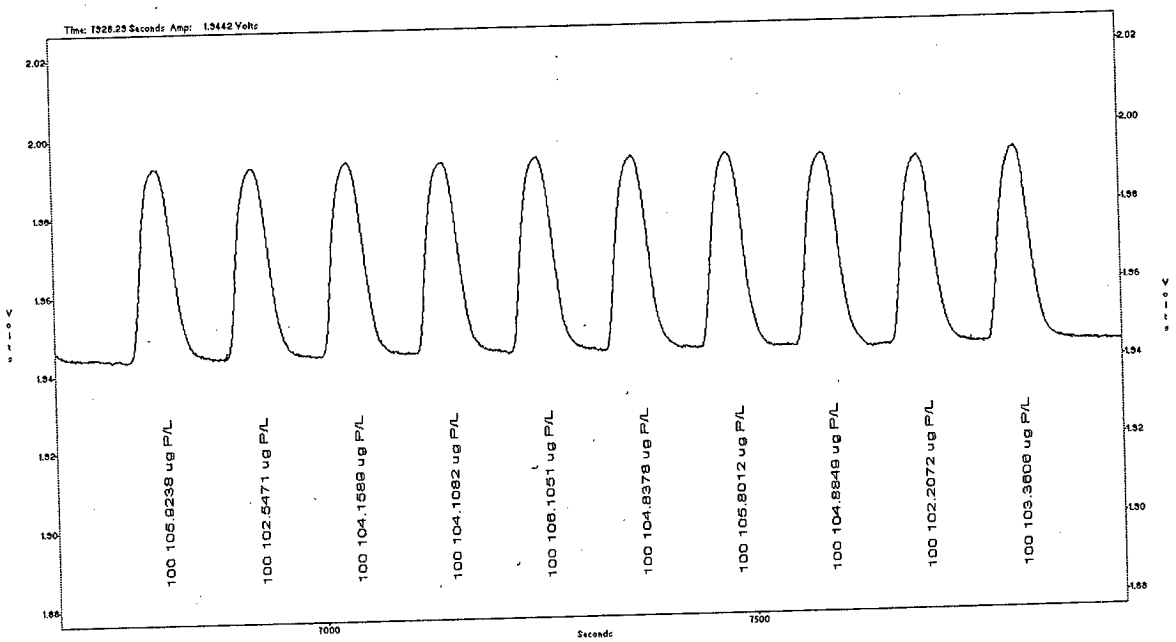

Method Detection Limit using 10 µg P/L as orthophosphate

**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:



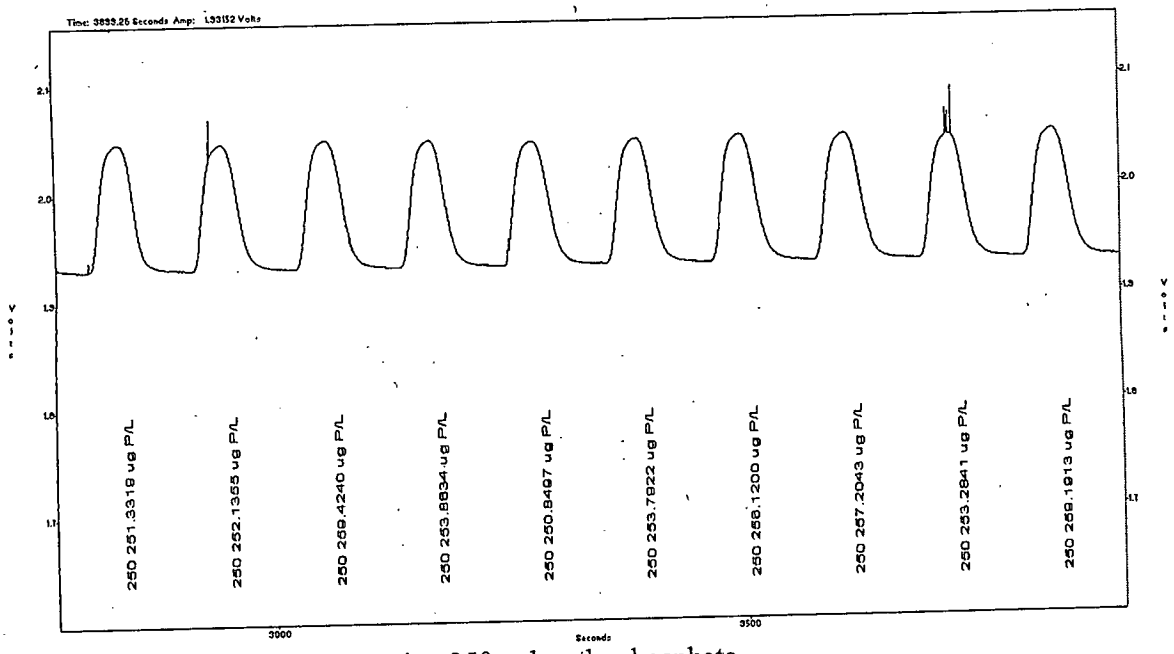

Precision data for phosphorus using 100 ppb orthophosphate

**%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:



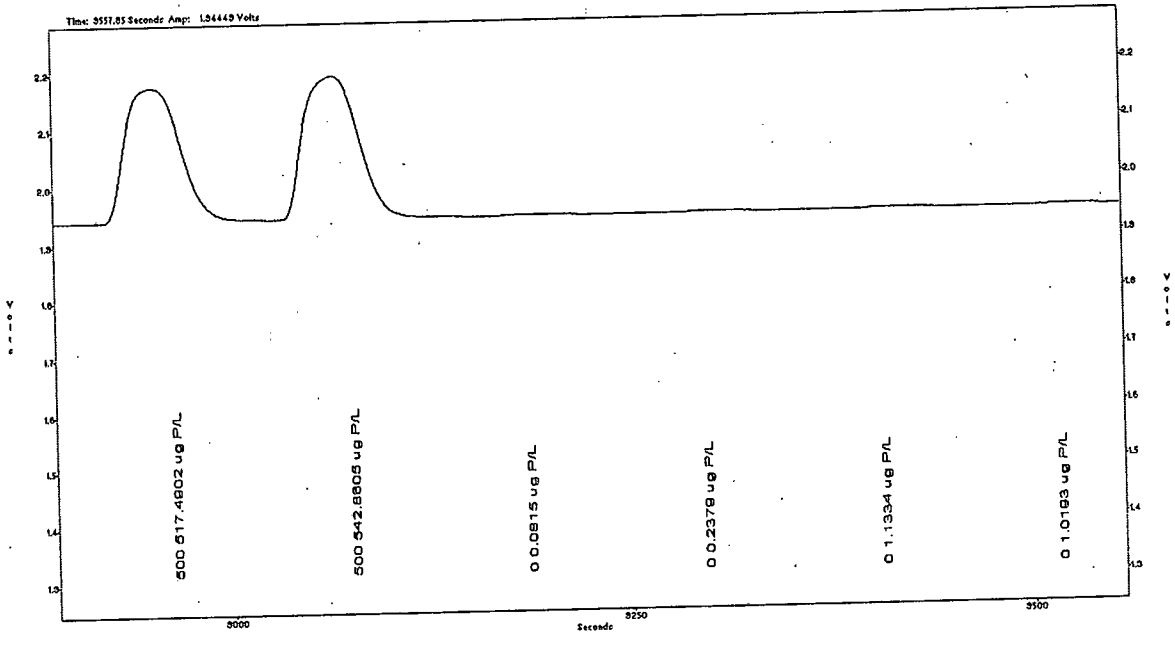

Precision data for phosphorus using 250 ppb orthophosphate

**%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:



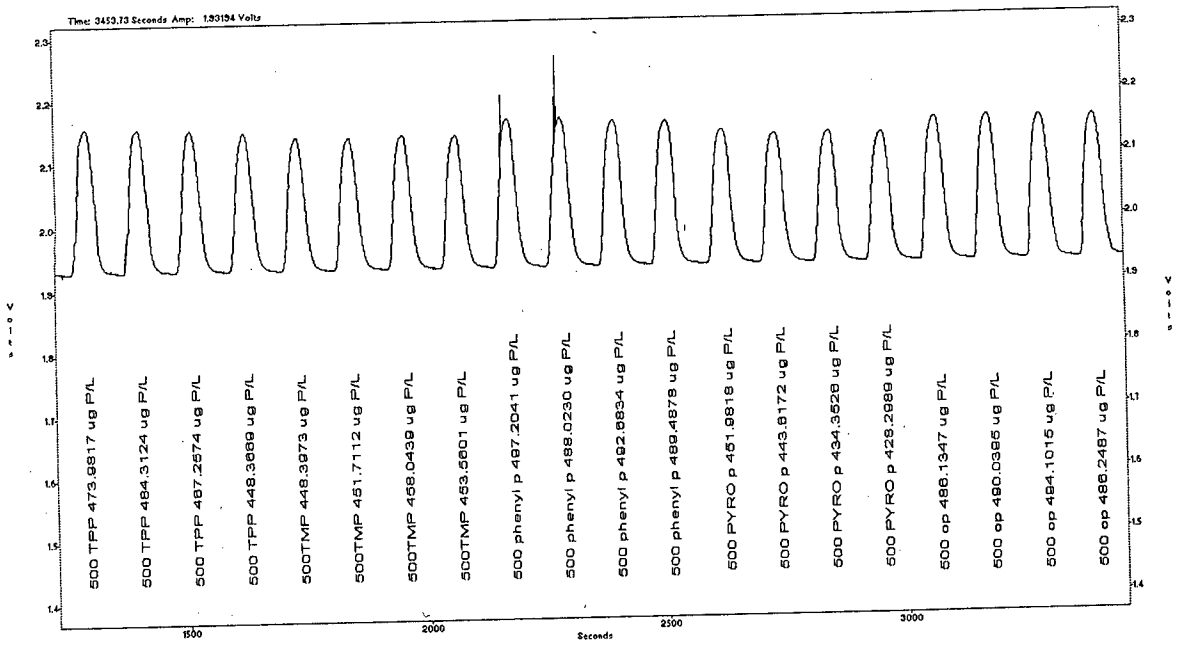

Carryover

**Carryover passed**

Data Filename: 042502E.fdt

Acq Date: 25 April 2002:

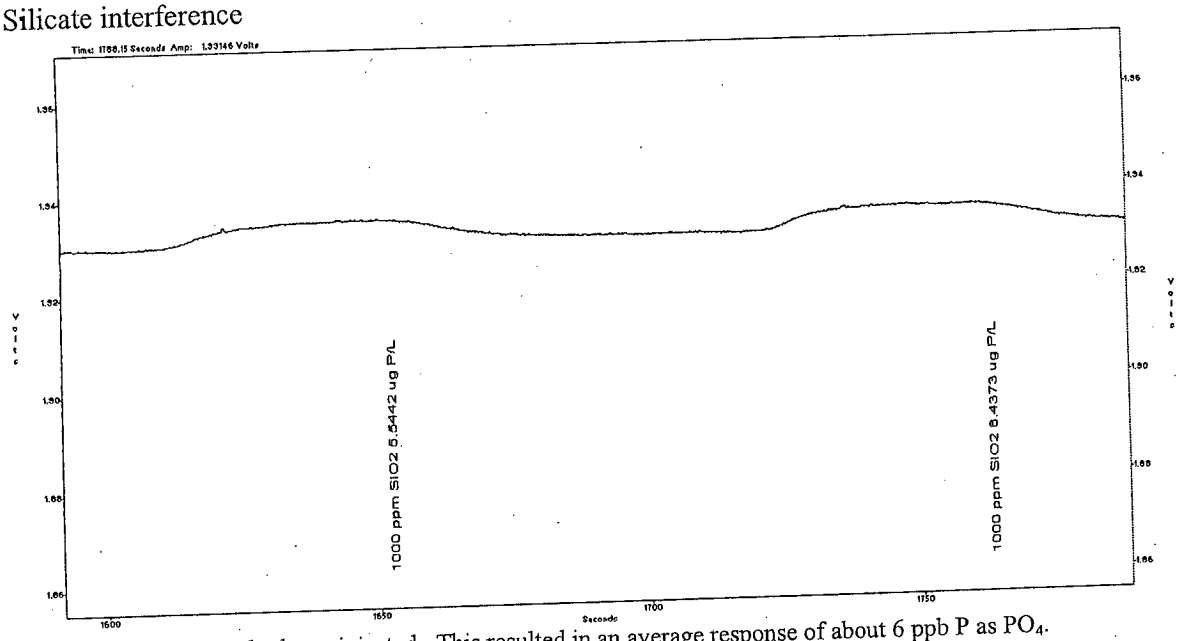
Recovery of Digestion Check Standards at 500 ppb




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

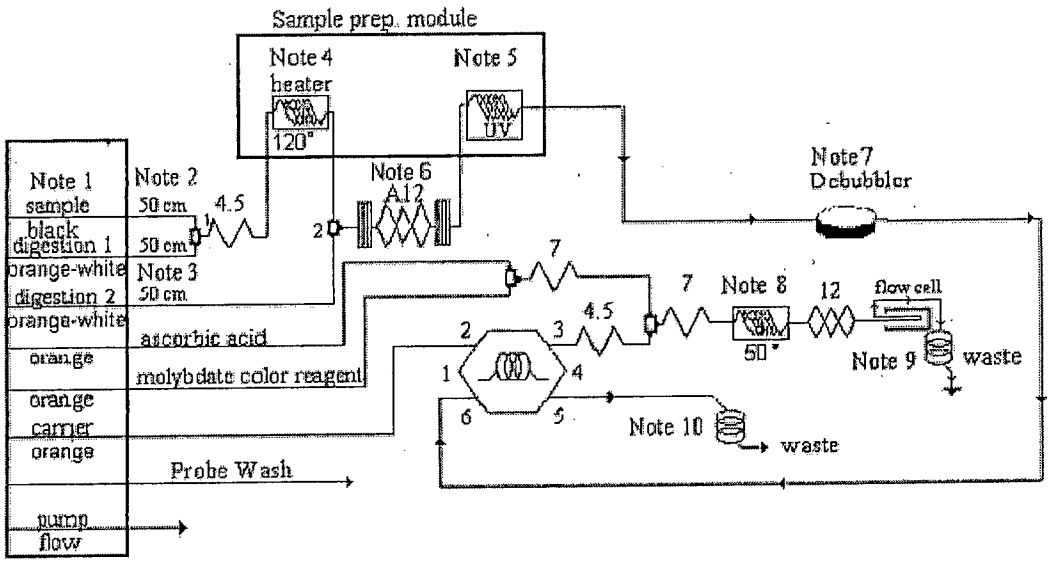
| Sample | Known Value, µg P/L | Determined value, µg P/L | % recovery, relative to orthophosphorus |
|---|---|---|---|
| **OrthoP** | --- | 489.13 | 100% |
| **TPP** | 500 | 468.48 | 95.77 |
| **Pyro P** | 500 | 439.56 | 89.87 |
| **Phenyl Phos** | 500 | 491.85 | 100.55 |
| **TMP** | 500 | 452.93 |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

Silicate interference



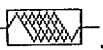

A 1000 ppm $SiO_2$ standard was injected. This resulted in an average response of about 6 ppb P as $PO_4$.
**Conclusion:** Silicate is not a significant interferent in this method. (Selectivity: 166,667)
Data Filename: 050102A.fdt
Acq Date: 01 May 2002

## 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

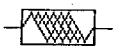
---

**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.

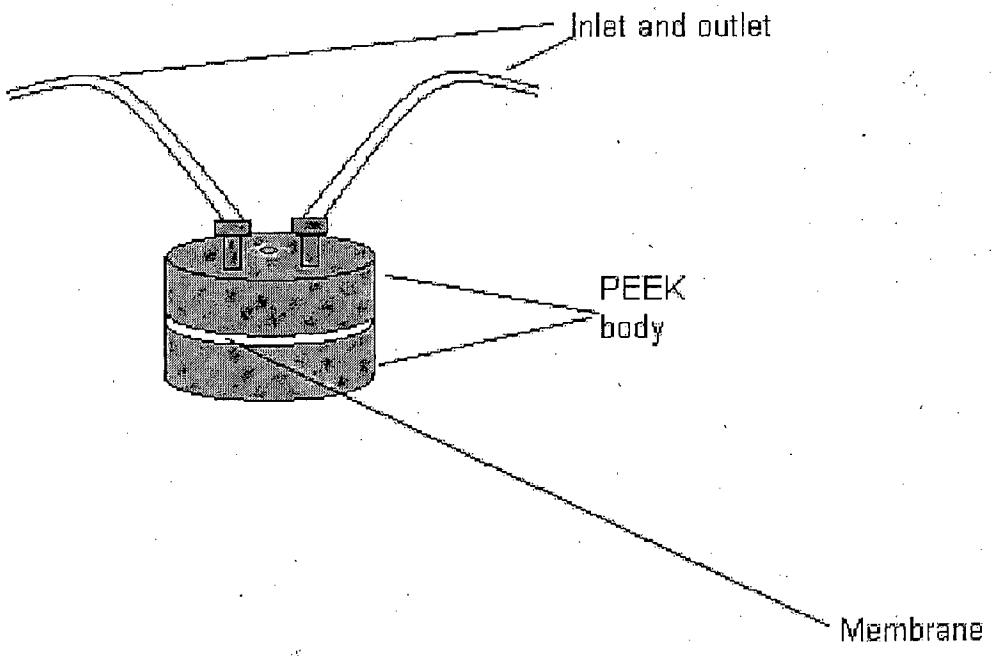
**Note 7:** **The Debubbler** is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing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

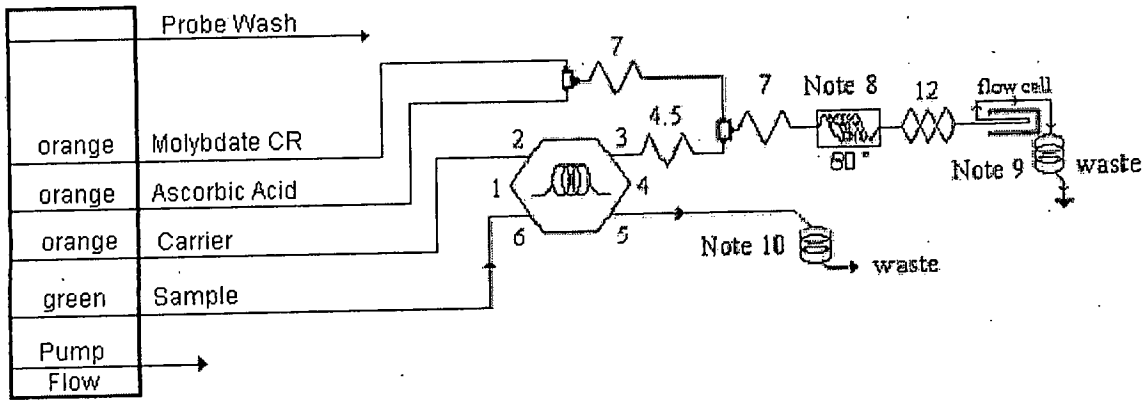
**Sampler Timing:**

| | |
|---|---|
| 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.

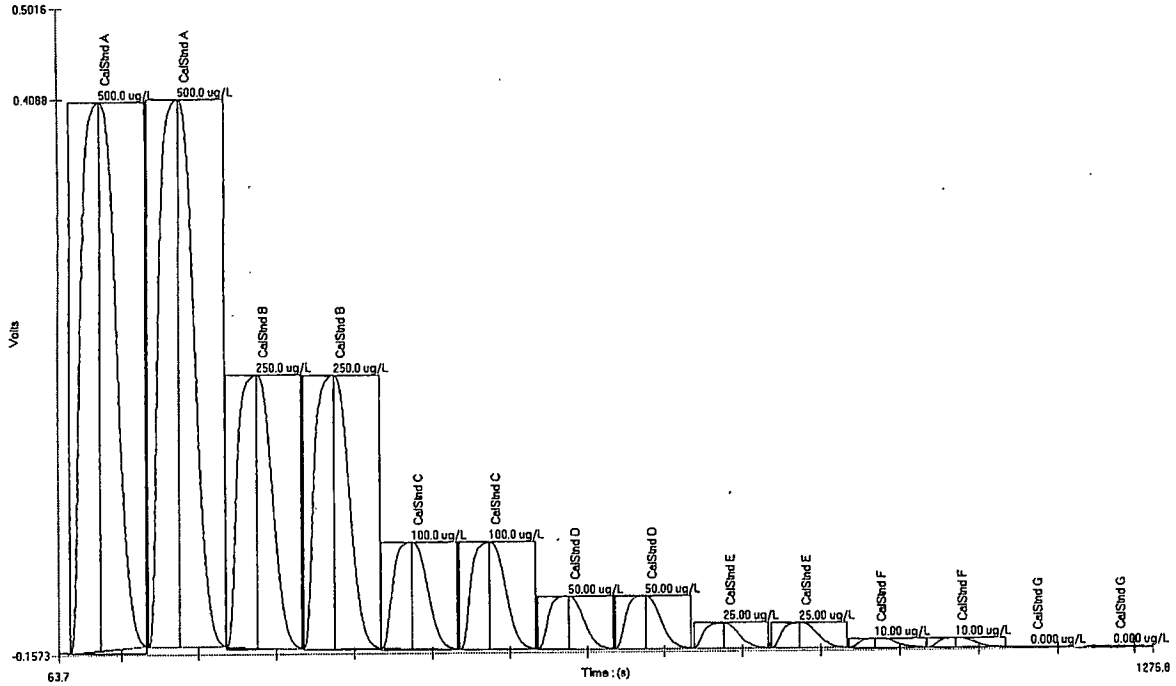
**4.5:** **70** cm of tubing on a 4.5 cm coil support
**7:** **135** cm of tubing on a 7 cm coil support
**12:** **255** cm of tubing on a 12 cm alternating coil support

---

**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

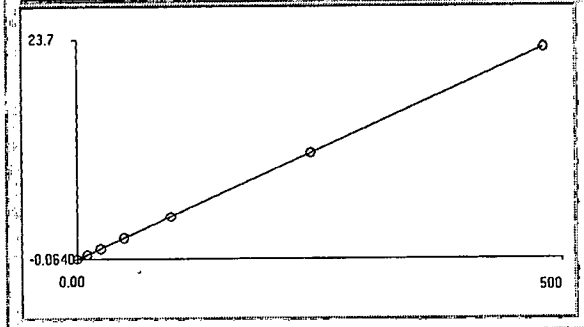



File Name: 12-3 cal support.omn
Acq. Date: 3 Dec 2010

## Calibration Graph and Statistics

Calibration Results - Channel 4

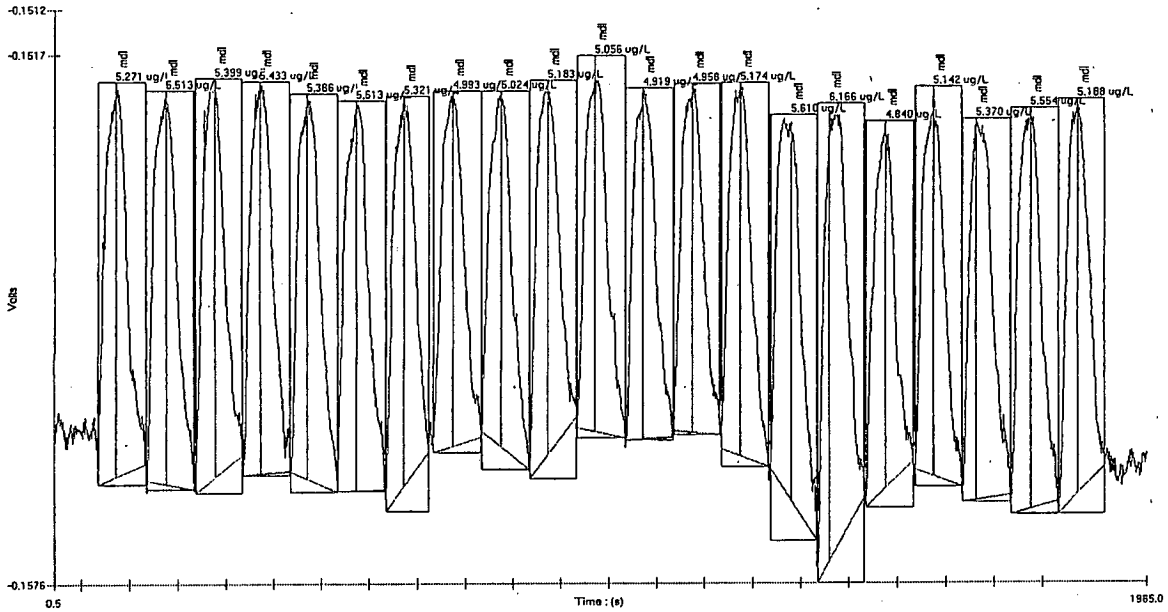
| | Known Conc. (ug/L) | Rep. | Peak Area (V.s) | Peak Height (V) | % RSD | % Resid. | Unused | Det. Conc (ug/L) | Date | Time |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 500.0 | 1 | 23.70 | 0.5598 | 0.2 | -0.2 | ☐ | 501.1 | 12/3/2010 | 7:19:49 AM |
| 2 | 500.0 | 2 | 23.64 | 0.5585 | 0.2 | 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



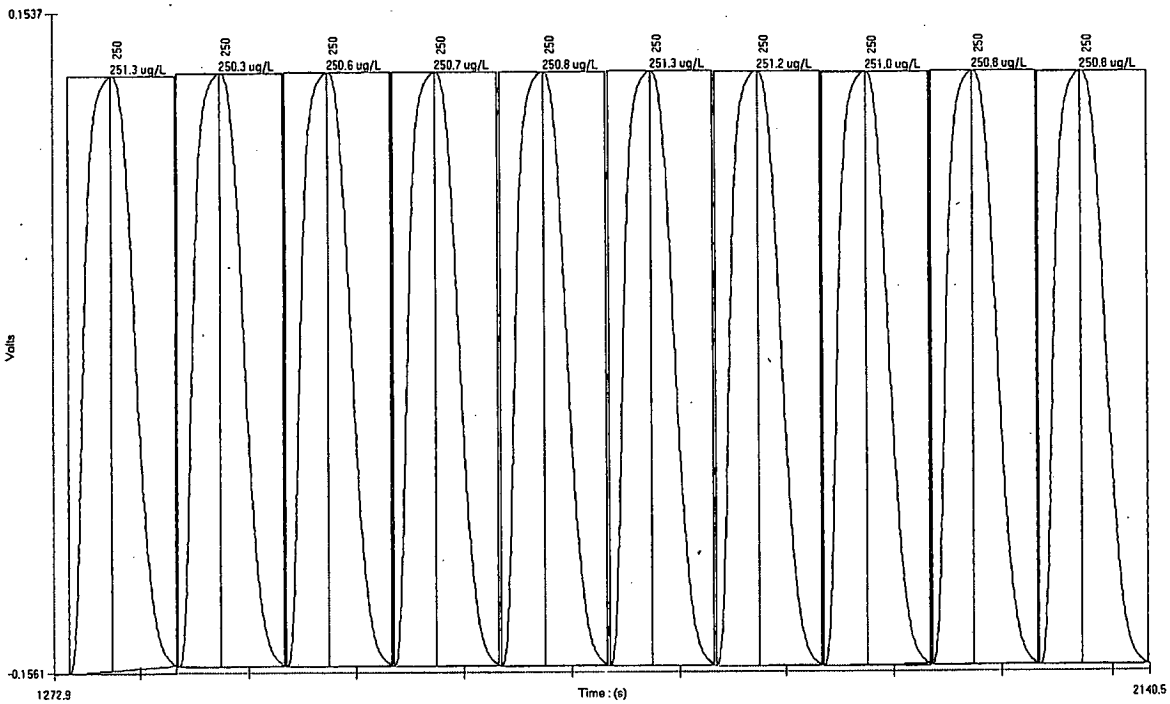

Method Detection Limit for Ortho Phosphate using a 5 µg P/L standard

**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



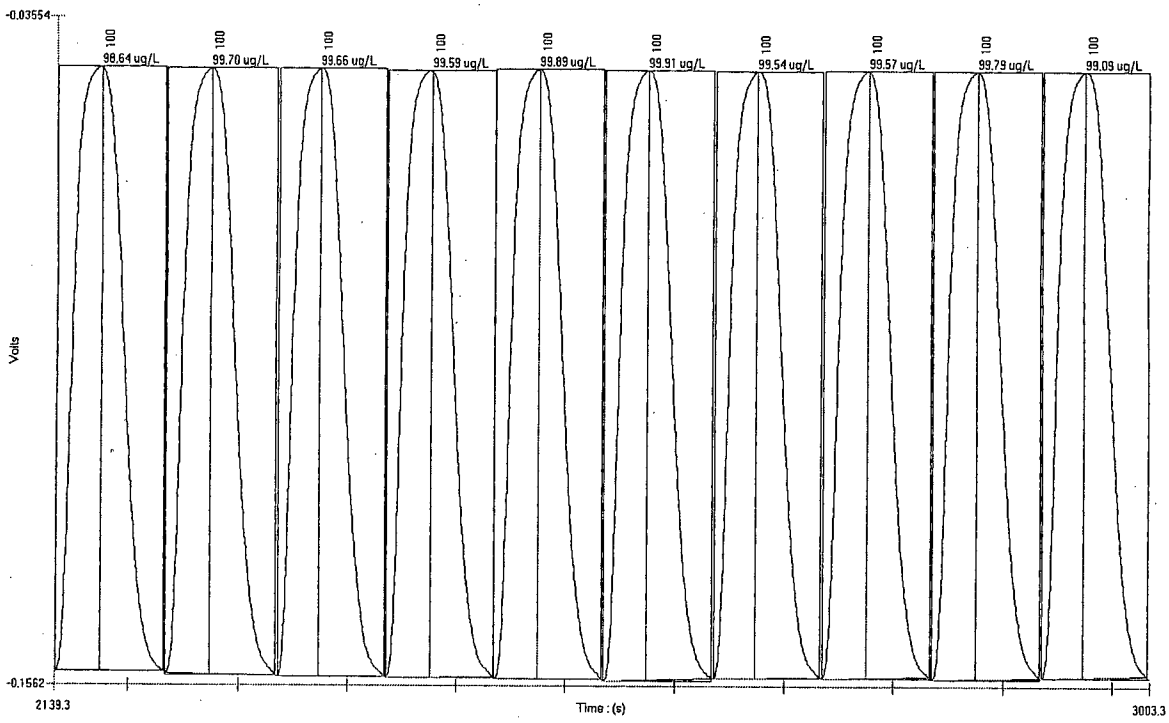

Precision Data for Ortho Phosphate using a 250 µg P/L standard

**% 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



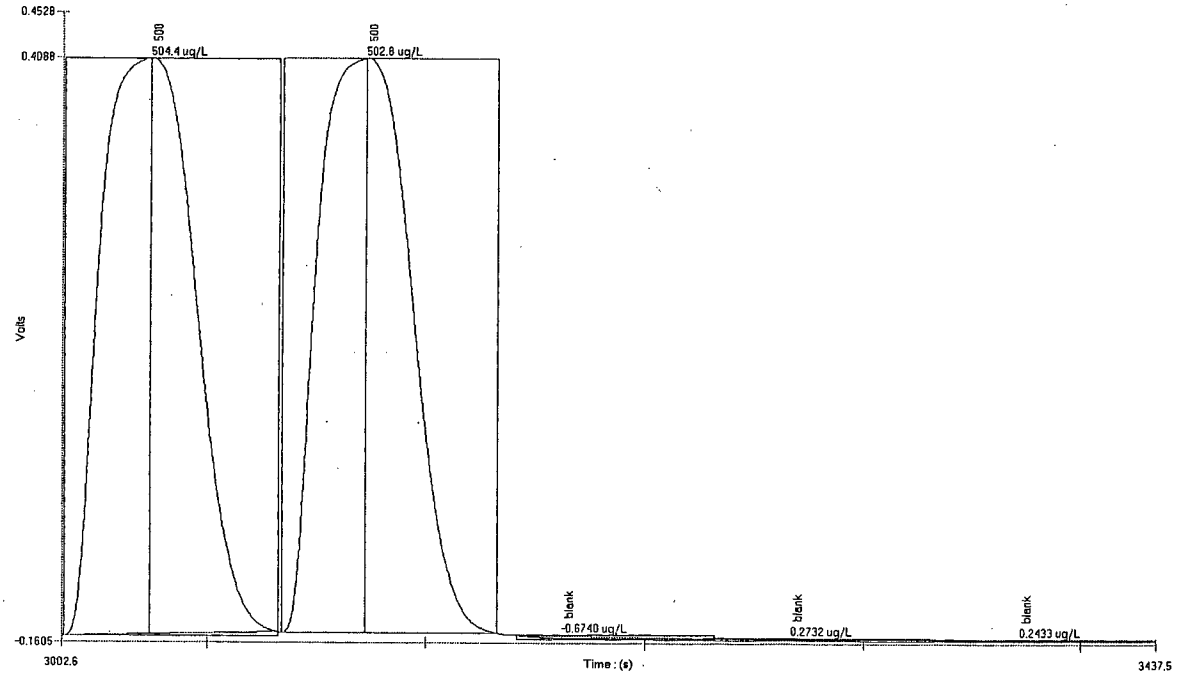

Precision Data for Ortho Phosphate using a 100 µg P/L standard

**% 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

| REVISION NUMBER | AUTHOR/ REVISOR | REVISION DATE | DESCRIPTION OF CHANGE |
|---|---|---|---|
| 0 | Dane Huber | 03-23-13 | This is the first release for a controlled, standardized format for General Chemistry. |

**PROCEDURE FOR THE DETERMINATION OF:**

# DISSOLVED SULFIDE IN WATER AND SOIL WITH INLINE DISTILLATION
BY
# FLOW INJECTION ANALYSIS COLORIMETRY

**Sulfide & Acid Volatile Sulfide**

## Table of Contents

**Section** **Page**

SCOPE AND APPLICATION

1.1 Sulfide is often present in groundwater, especially in hot springs. Its common presence in wastewaters comes from the decomposition of organic matter, industrial wastes, mine run off, and the bacterial reduction of sulfate. Hydrogen sulfide escaping into the air from sulfide-containing wastewater causes odor-nuisances. The threshold odor concentration of $H_2S$ in clean water is between 0.025 and 0.25 ug/L. Gaseous $H_2S$ is very toxic and has claimed the lives of numerous sewer workers. At levels toxic to humans it interferes with the olfactory system so that it cannot be detected. It attacks metals directly and indirectly has caused serious corrosion of concrete sewers because it is oxidized biological to $H_2SO_4$ on the pipe wall. Dissolved $H_2S$ is toxic to fish and other aquatic organisms.

1.2 Hydrogen sulfide, in sediments, can combine with iron and other metals to form slightly-soluble precipitates. Acid-volatile sulfides (AVS) is an main class of metal sulfides and is considered to be the key binding phase for controlling bioavailability of toxic metals in anoxic sediments.

1.3 This Standard Operating Procedure (SOP) is applicable to the measurement of sulfide in drinking, ground, and surface waters, and domestic and industrial wastes.

1.4 This SOP can be used for sample analysis under the Clean Water Act (CWA).

1.5 The working range is 0.01 to 2.0 mg/L. Dilutions are prepared for concentrations greater than 2.0 mg/L. The working range of the reference method is 0.01 to 2.0 mg/L.

1.6 This SOP is compliant with the requirements of SM4500-S2 E using the Lachat QuikChem® Method 10-116-29-3-A. Approval letters (Appendices I and II).

2.0 SUMMARY OF METHOD

2.1 The method is based on the methylene blue reaction.

2.2 Hydrogen sulfide ($H_2S$) is released by means of in-line distillation under acidic conditions. The gaseous $H_2S$ is separated by a diffusion cell, and then absorbed by a sodium hydroxide solution. The method does not recover sulfide from insoluble matter such as CuS or suspended solids.

2.3 The distilled hydrogen sulfide ($H_2S$) then reacts in acid media and in the presence of ferric chloride with two molecules of N,N-dimethyl-p-phenylenediamine to form methylene blue. The resulting color is read at 660 nm and is proportional to the concentration of $H_2S$ in the sample.

## 3.0 DEFINITIONS

3.1 Definitions that are common to all areas of the laboratory appear in the QA Manual.

## 4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in reagent water, solvents, reagents, glassware, and other sample processing apparatus that can lead to discrete artifacts, elevated baselines or that may otherwise bias analyte response. All reagents and apparatus must be routinely demonstrated to be free from interferences by analyzing a Method Blank (BLK) with each batch of no more than 20 samples.

4.2 Strong reducing agents at levels of several hundred ppm inhibit color formation.

4.3 Iodide interferes at levels greater than 2 mg/L.

4.4 The method is relatively free from interferences because gas dialysis separates the sulfide from sample matrix.

4.5 During sample collection, sulfide might be lost by oxidation reaction with air or oxidizing agents in sample, such as chlorine.

## 5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents and chemicals used in this SOP has not been fully established. Each chemical should be regarded as a potential health hazard, and exposure to these compounds should be as low as reasonably achievable.

5.2 Analysts who work in the lab are required to read the following MDH safety policies located in the MDH Policy and Procedure Manual:

| POLICY # | TITLE |
|---|---|
| 902.02.1 | Occupational Safety and Health |
| 420.01.1 | Right-to-Know |

5.3 In addition, the analyst should read the MDH Public Health Laboratory Division – Chemical Hygiene Plan (http://fyi.health.state.mn.us/phl/safety/index.html). Questions regarding the Chemical Hygiene Plan should be referred to the Laboratory Health and Safety Officer.

5.4 The analyst should read the Lab Building Emergency Procedures plan (http://fyi.health.state.mn.us/phl/safety/index.html) and know what to do in a variety of emergency situations.

5.5 Safety glasses should be worn by all analysts at all times while in the laboratory area. Visitors are given temporary safety glasses while in the laboratory. Lab coats and other protective clothing should be worn by analysts when appropriate.

5.6 The analyst may contact the Minnesota Poison Control System regarding employee exposures to hazardous chemicals (www.mnpoison.org or 1-800-222-1222). The system is available 24 hours per day, seven days per week.

5.7 The following chemicals have the potential to be highly toxic or hazardous; consult applicable MSDS.

5.7.1 Hydrochloric Acid

## 6.0 EQUIPMENT AND SUPPLIES

6.1 Balance – Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Glassware - All glassware must be borosilicate. Volumetric flasks and pipettes are Class A. All non-disposable glassware must be rinsed with 1:1 Hydrochloric acid (HCl) followed by three rinses with reagent water prior to use.

6.3 Fixed and adjustable pipettes.

6.4 Flow injection analysis equipment designed to deliver and mix samples and reagents in the required order and ratios (Lachat Instrument or equivalent).

6.4.1 Autosampler

6.4.2 Multichannel proportioning pump

6.4.3 Reaction unit or manifold

6.4.4 Colorimetric detector

6.4.4.1 Flow Cell: 10 nm, 80 µL.

6.4.4.2 Interference Filter: 660 nm

6.4.5 Omnion® software (version 3.0)

6.4.6 Printer

6.4.7 Lachat Special Apparatus

6.4.7.1 Heating Unit

6.4.7.2 PVC pump tubing must be used for this SOP

6.5 Disposable 13X100 mm test tubes (use once and discard)

6.6 Disposable 5ml safety lock syringe and needles (use once and discard)

6.7 Vortex mixer

6.8 Acid-Volatile

6.8.1 60 mL Teflon vials

6.8.2 33 mL Teflon transfer caps

6.8.3 0.125" OD x .062" Teflon tubing

6.8.4 Flow meters

6.8.5 Multi-position Stir Plate

6.8.6 High purity nitrogen

6.8.7 50 mL plastic digestion tubes and caps

6.8.8 Drying oven equipped with digital thermometer, for operation at 95° C and 180° C

6.8.9 Desiccating cabinet

6.8.10 Moisture indicating desiccant: Drierite: 97% $CaSO_4$ CAS# 778-18-9 and 3% $CoCl_2$ CAS#7646-79-9

6.8.11 Heat resistant trays

6.8.12 57 mm Aluminum weighing dishes or equivalent

6.8.13 Forceps

6.8.14 Stir plate

6.8.15 Balance data transfer software (i.e. Collect 6.1)

6.8.16 Excel spreadsheet template with proper calculations.

## 7.0 REAGENTS AND STANDARDS

7.1 Reagent Water: ASTM Type I or equivalent with resistivity > 16 mega ohm-cm at 25°C and free of the analyte sulfide.

7.2 Only Analytical Reagent (AR) grade or American Chemical Society (ACS) grade chemicals should be used.

7.3 Standardized 0.0250 N Iodine Solution: Purchased commercially.

7.4 Standardized 0.0250 N Sodium Thiosulfate Titrant: Purchased commercially.

7.5 Starch Indicator Solution 2% w/v: Purchased commercially.

7.6 Degassing with Helium: To help prevent bubble formation, reagent water used to make reagents should be degassed. Use 20 $lb/in^2$ through a helium degassing wand. Bubble He through the reagent water for at least 10 minutes.

7.7 Hydrochloric Acid, 3 M: In an acid-rinsed, 1-L volumetric flask, add 600 mL of degassed reagent water, then slowly add 248 mL of concentrated hydrochloric acid (HCl). Dilute to 1-L with degassed reagent water. Prepare fresh monthly.

7.8 Hydrochloric Acid, 0.20 M: In an acid-rinsed, 1-L volumetric flask, add 700 mL of degassed reagent water, then add 16.5 mL of concentrated hydrochloric acid (HCl). Dilute to 1-L with degassed reagent water.

7.9 Sodium Hydroxide, 0.025 M: In an acid rinsed, 2-L volumetric flask, add 2 g of sodium hydroxide (NaOH) to approximately 800 ml of degassed reagent water. Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh daily. This reagent is used for standards diluent and carrier reagent. Remake 2-L portions as needed.

7.10 N,N-Dimethyl-p-phenylenediamine Reagent: In an acid-rinsed, 1-L volumetric flask, dissolve 1.0 g N,N-Dimethyl-p-phenylenediamine

[$(CH_3)_2NC_6H_4NH_2 \cdot 2HCl$] in approximately 800 mL 3 M hydrochloric acid reagent. Stir until dissolved. Dilute to volume with 3 M hydrochloric acid reagent. Prepare fresh monthly. Degas if necessary.

7.11 Ferric Chloride Reagent: In an acid-rinsed, 500-mL volumetric flask, dissolve 6.65 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in approximately 450 mL 0.20 M hydrochloric acid reagent. Stir until dissolved. Dilute to volume with 0.20 M hydrochloric acid reagent. Prepare fresh monthly. Degas if necessary.

7.12 Digestion Solution: In an acid-rinsed, 1-L volumetric flask, add approximately 700 mL of degassed reagent water, then add 90 mL of concentrated phosphoric acid ($H_3PO_4$). Dilute to volume with degassed reagent water. Prepare fresh monthly. Degas if necessary.

7.13 Alkaline Antioxidant Reagent: In an acid rinsed, 500-mL volumetric flask, add approximately 300 mL of degassed reagent water, then add 40 g sodium hydroxide (NaOH), 17.5 g ascorbic, and 33.5 g disodium ethylenediamine tetraacetate dehydrate ($Na_2EDTA \cdot 2H_2O$). Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh monthly. Degas if necessary.

7.14 Zinc Acetate Preservative, 2N: In an acid rinsed, 200-mL flask, add approximately 100 mL degasses reagent water, then add 88 g zinc acetate dehydrate ($(Zn(O_2CCH_3)_2 (H2O)_2$). Stir until dissolved. Dilute to volume with degassed reagent water. Prepare fresh every 6 months.

7.15 NaOH preservative, 15 M: In an acid rinsed, 200-mL flask, add approximately 100 mL degassed reagent water, then add 125 g sodium hydroxide pellets (NaOH). Stir until dissolved. Dilute to volume with degassed reagent water.

7.16 Acid –Volatile Reagents

7.16.1 NaOH, 2N: In an acid rinsed, 500-mL flask, add approximately 300 mL degassed reagent water, then add 100 mL 10N NaOH. Dilute to volume with degassed reagent water. Prepare freshly each month.

7.16.2 Acid-volatile Catch Solution: In an acid rinsed, 500 mL flask, add approximately 300 mL degassed reagent water, then add 100 mL alkaline antioxidant reagent and 12.5 mL 2N NaOH. Dilute to volume with degassed reagent water. Prepare freshly daily.

7.16.3 Hydrochloric Acid, 9N: In an acid rinsed, 250 mL flask, add approximately 100 mL degassed reagent water, then slowly add 186 mL concentrated hydrochloric acid. Dilute to volume with degassed reagent water.

7.16.4 Stannous Chloride Solution, 0.53M: Dissolve 50 g $SnCl_2$ into 250 mL 9N HCl solution.

7.17 Calibration Standards:

7.17.1 Stock Standard (100 mg/L): In an acid-rinsed, 1-L volumetric flask, dissolve 0.7491 g sodium sulfide nonahyrdate ($Na_2S \cdot 9H_2O$, Mallinckrodt 8044 or equivalent) in approximately 900 mL of 0.025 M sodium hydroxide reagent. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily. Standardize this stock standard after preparation.

7.17.1.1 In an acid rinsed, 250-mL Erlenmeyer flask, add 20 mL 0.0250 N iodine solution and 2 mL 1:1 HCl.

7.17.1.2 Add 10 mL of 100 mg/L stock standard.

7.17.1.3 Titrate with 0.0250 N sodium thiosulfate until a straw yellow color appears.

7.17.1.4 Add a few drops of 2% w/v starch indicator (mixture will turn blue) and continue titration until blue color disappears.

7.17.1.5 Calculate the concentration of stock standard using the following calculation

$$[((A \times B) - (C \times D)) \times 16000] / \text{mL sample} = \text{mg/L sulfide}$$

Where: A = normality of iodine solution

B = mL of iodine solution used

C = normality of thiosulfate solution

D = mL of thiosulfate used

7.17.1.6 Two blanks should be run to verify the normality of iodine and sodium thiosulfate has not changed.

7.17.1.7 Using the found concentration of the stock standard, determine the volume of stock standard needed to make the 10 mg/L intermediate standard. The formula used is $C_1V_1 = C_2V_2$.

7.17.2 Intermediate Stock Standard (10 mg/L): In an acid-rinsed 500-mL volumetric flask, add the volume of 100 mg/L stock standard determined in 7.14.1.7. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily.

7.17.3 Working Calibration Standards: To prepare 200 mL quantities of calibration standards, use acid-rinsed, 200-mL volumetric flasks. Add 20 mL of alkaline antioxidant reagent to approximately 100 mL of 0.025 M sodium hydroxide reagent. Use the table below to determine the correct amount of stock standard to pipette into each volumetric flask. Dilute to volume with 0.025 M sodium hydroxide reagent and invert to mix. Prepare fresh daily.

| Calibration Standard | Quantity of 10 mg/L Intermediate Stock Standard |
|---|---|
| 2.0 mg/L | 40 mL |
| 1.0 mg/L | 20 mL |
| 0.50 mg/L | 10 mL |
| 0.1 mg/L | 2 mL |
| 0.05 mg/L | 1 mL |
| 0.02 mg/L | 0.4 mL |
| 0.01 mg/L | 0.2 mL |
| 0.0 mg/L | — |

7.18 The second-source calibration verification (SCV) is purchased and prepared according to instructions provided by the manufacture. Use 0.025 M sodium hydroxide reagent as diluent and add alkaline antioxidant reagent at 10% of final volume.

7.19 1:1 Hydrochloric Acid: Add an equal volume of concentrated HCl (37%) to reagent water. This reagent is prepared by designated laboratory personnel and used to acid rinse glassware.

7.20 All reagents should be discarded if precipitate or growth appears.

7.21 All reagents and standards are verified as described in Section 9.6.

## 8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 Samples are collected in 125 mL glass serum bottles and stored at 4°C ± 2°C prior to analysis.

8.2 Bottle preservation and preparation

8.2.1 0.2 mL Zinc Acetate preservative, 0.5 mL sodium hydroxide (NaOH) preservative, and magnetic stir bar are added to each serum bottle.

8.2.2 Each bottle is purged with high purity nitrogen gas for 30 seconds and capped with a 20 mm septum stopper and a 20 mm tear off seal.

8.2.3 Each bottle is then weighed, using an analytical balance, and initial weight is recorded on label of bottle.

8.2.4 After samples are collected, bottles are weighed, using an analytical balance, and weight is recorded on label of bottle.

8.2.5 Using a Safety-Lok syringe, 5-6 mL of Alkaline Antioxidant Reagent is injected into each bottle.

8.2.6 Bottles are placed on stir plate, for at least 1 hour to dissolve any particulate.

8.2.7 Each bottle is weighed a 3rd time, using an analytical balance, and final weight is recorded on label of bottle.

8.2.8 All weights are recorded in Element bench sheet.

8.3 Maximum holding time is 14 days when stored at 4°C ± 2°C.

8.3.1 Holding time for Acid Volatiles is 6 months when preserved with Zinc Acetate and stored at -20 °C.

## 9.0 QUALITY CONTROL

9.1 Initial Demonstration of Capability (IDC): The analyst must be able to demonstrate that they can generate acceptable accuracy and precision data with this SOP by successful completion of the following:

9.1.1 Initial Calibration: The 1st order calibration range must be determined initially and whenever a significant change in instrument response is observed. The initial demonstration of linearity must use a calibration blank and a minimum of 3 different calibration standards. One of the standards is near, but above the MDL. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion. The standards must bracket the range of concentrations found in samples and should define the working range of the instrument.

9.1.2 External Verification of Calibration: A second-source calibration verification standard (SCV) from an external source is analyzed. The results of the SCV must be within the manufacturer's certified range of the established SCV value, otherwise remedial action is taken and the entire Initial Demonstration of Capability is repeated.

9.1.3 Method Detection Limit (MDL) Study: A minimum of 7 replicate Laboratory Control Samples (BS) are spiked at a value 1 to 5 times the estimated detection limit and processed over a period of three days. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. MDLs must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated. Once the IDC has been established for this SOP, the Unit Supervisor may waive this requirement for individual analysts if the reference method does not specifically require an MDL study for new analysts.

9.1.4 Initial Precision and Accuracy: To establish the ability to generate results with acceptable accuracy and precision, analyze 4 replicates of a mid-range standard. Calculate the mean concentration and the standard deviation for the data set. The percent recovery of the mean must be between 95% and 105%, while the percent relative standard deviation (%RSD) must be less than 10%. Both conditions need to be satisfied before sample analysis can begin.

9.1.5 Where this documentation is not available, the Quality Assurance Officer can establish other criteria to measure accuracy and precision for each analyst and each method.

9.1.6 Demonstration of Low Background: Analyze at least one Method Blank (BLK) to determine reagent or laboratory contamination. The BLK result must meet the criteria established for the on-going demonstration of low background in Section 9.2.3.

9.1.7 Other Requirements for an IDC: An IDC may also be required if there are significant changes to the SOP, matrix, or instrument that could affect the precision, accuracy or sensitivity of the analysis. Consult with the Quality Assurance Officer (QAO) to determine if any changes require an IDC.

9.1.8 IDC Documentation: An IDC for each analyst must be on file in the QA office along with an IDC for the method, matrix, and instrument.

9.2 Ongoing demonstration of acceptable performance: With every analytical run, the laboratory must perform the following:

9.2.1 Daily Calibration: Calibrate the instrument at the beginning of the analytical run or whenever the curve verification fails. Calibrate the instrument with a calibration blank and 7 standards covering the range of sample results and within the Linear Calibration Range (LCR) of the analyte. The curve used must be 2nd order polynomial and not forced through zero. Acceptable correlation coefficient for the calibration curve is 0.9990 or greater. The concentration of the calibration standards must be ±

10% of the true value, and ± 20% of the true value for the lowest standard. This corresponds to the percent residual calculation. The Calibration Statistics display on the analysis report summarizes in algebraic form what is seen graphically. The first equation shows the plotted calibration equation in the form of **Area f (Conc.)**, where the peak area is a function of **Conc.** or determined concentration of the analyte. The second equation is the same calibration equation, but solved for concentration. It is in the form **CONC = f (Area)**. This is the equation that is used to determine the concentration of unknowns. The third statistic is the value of **r**, the 'correlation coefficient' for the calibration.

9.2.2 External Verification of Calibration: Analyze a second source calibration verification (SCV) from the external source immediately after calibration to verify instrument performance. The results of the SCV must be within the manufacturer's range of the target value; otherwise corrective action is taken before analyzing samples. If the SCV is out of control, the run data can only be accepted by the Unit Supervisor.

9.2.3 Demonstration of Low Background: At the beginning of each run and with each batch, analyze an initial calibration blank (ICB) or blank (BLK) to determine reagent or laboratory contamination. The background level of the BLK or ICB must be below the report level; otherwise the source of the contamination is investigated and corrected before samples are analyzed. Analyze a continuing calibration blank (CCB) every 10 samples and at the end of the run. The CCB must be less than the report level (MRL). If the CCB is above the Report Level, the source of the deviation is investigated and corrected before the next batch of samples can be analyzed. Samples must be bracketed by passing CCBs to be accepted. Samples associated with failing CCBs are reanalyzed.

9.2.4 Report Level Verification (RLV) Check: A Report Level Verification (CRL) check must be performed each time the instrument is calibrated. The CRL check is performed by

analyzing a calibration standard at or below the report level (0.01 mg/L). (The CRL check sample is not required to be processed through the entire SOP.) The percent recovery of the CRL must be within ± 40%.

9.2.4.1 If the percent recovery of the CRL is outside the acceptance criteria, the analyst must either: 1) repeat the CRL or 2) recalibrate and then perform the CRL. If the repeat CRL is within acceptance criteria, or if the instrument recalibration results in a CRL that is within acceptance criteria, the analyst may proceed with the analytical run. If the CRL is not within acceptance criteria, the analyst must either: 1) recalibrate the instrument and then perform the CRL once again, or 2) perform the CRL at a higher concentration level.

9.2.4.2 If an acceptable percent recovery can only be achieved at a higher concentration level, the analyst must elevate the Report Level for the associated samples to the concentration of the lowest point that meets the acceptance criteria. The analyst must report all samples analyzed after the failed CRL using the elevated Report Level until a new calibration curve and CRL meet the acceptance criteria.

9.2.5 Continuing Verification of Calibration: Analyze a continuing calibration verification standard (CCV) after every 10th sample and at the end of the sample run. Each analyte must fall within ± 10% of its expected value. If an analyte is outside the interval, CCV is reanalyzed. If the analyte is still outside the ± 10% limit, the instrument is recalibrated and all samples following the last acceptable CCV solution are reanalyzed.

9.2.6 Accuracy: With every batch of 20 samples processed as a group, analyze a laboratory control sample (BS). Accuracy (as percent recovery) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Found Concentration of BS}}{\text{True Concentration of BS}} \times 100$$

9.2.7 If the recovery of the analyte falls outside the required control limits of 90-110%, the analyte is judged out of control. The source of the problem should be identified and the situation resolved before sample analysis can continue.

9.2.8 Matrix Effect: Run a matrix spike (MS) with each batch of 20 field samples processed as a group, or 5% of the samples analyzed, whichever is greater. The same solution used to fortify the BS is used to fortify the MS. Accuracy (as percent recovery after background correction) is calculated as follows:

$$\% \text{ Recovery} = \frac{\text{Concentration of MS - Concentration of Matrix Sample}}{\text{True Concentration of MS}} \times 100$$

9.2.9 If the recovery of the MS falls outside of 80-120% limits, the MS is repeated. If the recovery of the repeat analysis also falls outside the control limits, the possibility of matrix effects is investigated by analyzing a diluted sample that has been fortified. If the recovery of the analyte still falls outside the designated MS recovery range and the BS, and ICV/CCV for that analyte is shown to be in control, the recovery problem encountered with the MS is judged to be matrix induced and the results for the diluted sample and the MS are reported using an elevated report level reflective of the dilution used and the qualifier QD: "Recovery in MS not within acceptance limits" is added to the MS.

9.2.7.1 If the MS recovery of the diluted sample is within acceptable limits, the sample is reported with an elevated Report Level reflective of the dilution used.

9.2.10 Precision: Analyze a laboratory duplicate (DUP) with each batch of field samples processed as a group, or10% of the field samples analyzed, whichever is greater. Calculations of the

absolute difference between the duplicates and the relative percent difference (RPD) between the duplicates are used to monitor the precision of the method. Current control limits for precision are on file in the laboratory. If either the difference or the RPD for a set of duplicates falls outside of the applicable control limits, the reason for the out of control condition is investigated and the duplicate analyses are repeated.

9.2.10.1 Calculate the relative percent difference of the duplicates using the following formula:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = concentration of sample

D = concentration of duplicate sample

9.2.10.2 Duplicate acceptance criteria:

| Concentration Range | Criteria: |
|---|---|
| RL to 10xRL | None |
| 10xRL to highest calibration std | RPD $\leq$ 10% |

9.2.10.3 If the duplicate concentration is between the RL and 10xRL, and the RPD is greater than 10%, the qualifier QH is added to the duplicate: "RPD between sample duplicates not within acceptance limits. Analyte concentration in the samples too low for proper evaluation."

9.2.10.4 If the duplicate fails to meet the above criteria, the samples should be reanalyzed to verify poor duplicate analysis RPD. If the repeated duplicate is still not within acceptable limits, the samples must be reported with a qualifier identifying the sample analysis result as yielding poor duplicate analysis RPD.

9.3 External verification of laboratory performance: Proficiency Test (PT) samples are analyzed as required for Federal certification. If the results are not within acceptance criteria, corrective action is taken and an "Unacceptable Data for Performance Evaluation Samples" form is filled out by the analyst describing the probable error and any corrective action taken. The "Unacceptable Data" form is given to the Unit Supervisor and Laboratory Quality Assurance Officer.

9.4 The MDL study is repeated when changes in instrumentation or instrument response occur. A minimum of 7 replicate Laboratory Fortified Blanks (LFB) or 7 Report Level Verification (CRL) checks are spiked at a value 1 to 5 times the estimated detection limit and, ideally, analyzed over a period of at least 3 days. If necessary, the study may be conducted over a shorter period of time. The MDL is determined using the procedure in 40 CFR, Part 136, Appendix B. (See Section 16.3) MDL's must be low enough for regulatory/client purposes, otherwise remedial action is taken and the process is repeated.

9.5 Dissolved Analysis: The filtration blank results must be below the Report Level. If the filter blank is above the Report Level, consult with a lead worker or supervisor to determine if the filter blank result should be subtracted from the sample results or if other action should be taken.

9.6 Reagent and Standard Verification: All reagents and standards are verified prior to sample analysis by the analysis of ICV, ICB, SCV, CRL, CCV and CCB. Acceptable QC results along with an acceptable calibration curve demonstrate that all reagents and standards are verified for use.

## 10.0 CALIBRATION AND STANDARDIZATION

10.1 Prepare a series of 7 calibration standards and a calibration blank by diluting suitable volumes of calibration standard solution, as described in Section 7.16.

10.2 Set up the manifold as shown in Section 17. If necessary, refer to the Lachat manual for instrument operation.

10.3 Process calibration standards and calibration blank and calibrate the instrument as described in Section 11. Read calibration standards and calibration blank in descending concentration on the Lachat.

10.4 Prepare calibration standard curve by plotting instrument response against concentration value. The curve used must be 2$^{nd}$ order polynomial and not

forced through zero. The calibration standard curve will be fitted to the calibration standard solutions concentration/response data by the Omnion® 3.0 Software. Attach a pdf of the curve to the sequence in Element to document the initial calibration. The calibration standard curve is accepted if a correlation coefficient of at least 0.9990 is achieved. Also the concentration of the standards must be within ± 10% of their true value except the lowest standard which can be ± 20% of its true value.

10.5 After the calibration has been established, it must be verified by the analysis of the ICV, ICB, SCV, CRL, CCV and CCB.

10.5.1 If measurements exceed ± 10% of the established ICV value (0.5 mg/L), the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.2 The background level of the analyte in the ICB must be at or below the MDL; otherwise the source of the contamination is investigated and corrected before samples are analyzed.

10.5.3 The results of the CRL must be within ± 40% of the true value (0.01 mg/L) in order to proceed. If it is not, follow the procedure outlined in Section 9.2.4.

10.5.4 If measurements exceed the range of the established SCV value, the analysis should be terminated and the instrument recalibrated. The new calibration curve must be verified before continuing analysis.

10.5.5 A continuing calibration verification standard (CCV) and a continuing calibration blank (CCB) must be run every 10 samples and at the end of each run. The results for the CCB must be less than the report limit of 0.01 mg/L. The results for the calibration verification standard (CCV) must be within ± 10% of the true value (0.5 mg/L). If analytical results do not meet the above criteria, the analysis is terminated, the instrument is checked, and then re-calibrated. All samples following the last passing blank and standard are reanalyzed.

## 11.0 PROCEDURE

### 11.1 System Start-up

11.1.1 Set up manifold as shown in Section 17.2 and inspect manifold for proper connections.

11.1.2 Turn on power strip. Allow at least 15 minutes for the heating unit to warm up to 65°C. Do not pump reagents or water into the flow system until the temperature has reached 65°C.

11.1.3 Raise tension levers on pump tube cassettes. Place reagent lines into reagent water and check for leaks and smooth flow. Allow about 20 minutes for heater to reach equilibrium.

11.1.4 Transfer lines to designated reagent. Allow system to equilibrate until a stable baseline is achieved.

11.2 Prepare a BS and MS for each batch by adding 100 µL of Intermediate Stock Standard (10 mg/L) into a 10 mL borosilicate test tube. Add 5.0 mL of 0.0 mg/L blank solution or field sample. The true value is 0.2 mg/L.

11.3 Prepare a CRL by using the lowest non-zero standard, 0.01 mg/L. Pour approximately 5 mL of the 0.05 mg/L standard into a 10 mL borosilicate test tube.

11.4 Calibration and Sample Analysis

11.4.1 Prepare standards as described in Section 7.

11.4.2 Place calibration standards in descending order in the auto sampler standards tray. Select the default Sulfide template from the Sulfide data folder and input the information required by the data system, such as concentration, replicates, and QC scheme. Verify peak timing and integration parameters as specified in Section 17.3. Import the sequence ID numbers from Element Database.

11.4.3 Pour approximately 5 mL of each type of quality control and sample into a 10 mL borosilicate test tube and place in sample tray.

11.4.4 The CCV and CCB must be set up every 10 samples and at the end of each run in the template. The CCV is the 0.5 mg/L calibration standard. The CCB is the same as the calibration blank. The CCV and CCB come from the same cup as the equivalent calibration standard. Input the information required for the QC scheme. See Section 17.

11.4.5 Add approximately 5 mL of each properly preserved and prepared sample, filter blank, or sample aliquot diluted to 5 mL, into corresponding 10 mL borosilicate test tubes and place in sample tray. Set up 1 DUP for every 10 samples, and a BS and MS for every 20 samples.

11.4.5.1 After preservation and preparation, samples must be extracted from glass bottles using safety lock syringes. Discard locked syringe and needle in sharps container.

11.4.6 Calibrate the instrument by injecting standards. The data system will then associate the concentrations with the instrument responses for each standard and evaluate the curve.

11.4.7 After acceptable curve is achieved and initial QC is obtained and acceptable, continue with analysis.

11.5 System Shut Down

11.5.1 At the end of the run place all reagent lines into water to rinse for 15 minutes. Pump air through the manifold for 30 minutes to dry the distillation system, especially the membrane. Keep the heater at 65°C until 30 minutes of air drying is complete.

11.5.2 Turn off the pump and the power strip. Release the tension levers on the pump tube cassettes.

11.6 System and Procedure Notes

11.6.1 For information on system maintenance and troubleshooting refer to the Troubleshooting Guide in the System Operation Manual (Guide is also available on request from Lachat). Consult the Instrument Book for the Lachat systems for current information on preventative maintenance procedures.

11.6.2 Samples that are over concentrated should be diluted with the diluent and not reagent water.

11.7 Acid-Volatile Samples

11.7.1 Allow samples to thaw to room temperature.

11.7.2 Using an analytical balance, weigh out 1 g of soil into Teflon vial. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors.

11.7.3 Add 25 mL Acid-volatile catch solution to each 50 mL trap and label each with specified sample number.

11.7.4 Set flow meters to a scale reading of 20. Loosely cap each Teflon vial and allow nitrogen to purge for at least three minutes.

11.7.5 Using a syringe, inject 15 mL stannous chloride solution into each Teflon vial. Quickly screwing on each cap so that no sulfide is lost.

11.7.6 Turn on stir plate and allow nitrogen to purge at room temperature for 3 hours.

11.7.7 After 3 hours remove 2.5 mL of sample and dilute with 2.5 mL of diluent and proceed to step 11.4.3.

11.8 Acid-Volatile dry weight

11.8.1 Allow samples to thaw to room temperature.

11.8.2 Tare the balance. Open the Acid-Volatile dry weight spreadsheet template. Enter dish numbers in spreadsheet. Open balance data transfer program and select Acid-Volatile method.

11.8.3 Place dish on balance. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors

11.8.4 ***When preparing Acid-Volatile solids it is essential that you mix the sample well.*** Using an analytical balance, weigh out 5 g of soil into. When balance stabilizes, record weight in spreadsheet. Data transfer program will insert weight in selected spreadsheet cell, eliminating need for typing weight and the possibility of transcription errors.

11.8.5 Set up a Duplicate (DUP) and for every 10 samples.

11.8.6 Place sample in 105° C for at least 12 hours. Remove dishes from oven using heat resistant gloves and tongs; allow dishes to cool on the bench top for no more than 10 minutes (set timer). Complete cooling to room temperature in desiccator.

11.8.7 Record dish weights using an analytical balance, computer, software and Excel spreadsheet enter dry weight in Element.

## 12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Calibration is accomplished by injection of standards. The data system will then prepare a calibration curve by plotting instrument response versus standard concentration. Sample concentration is calculated from the regression equation. Multiply results by appropriate dilution factor.

12.2 The method detection limit (MDL) is calculated as described in Section 9.4. The current MDL value is on file in the QA Office.

12.3 The minimum report level is 0.01 mg/L.

12.4 Results are reported in mg/L to three significant figures.

12.5 Sample results and quality control data are transferred electronically to the Element Database for review by the analyst.

12.6 Report only those values that fall between the lowest and highest calibration standard. Samples exceeding 2.0 mg/L are diluted and reanalyzed.

12.7 Results reports are reviewed by Unit Supervisor or designee according to established procedure prior to transmittal to client.

## 13.0 PERFORMANCE

13.1 Information pertinent to our laboratory's performance is available in the QA Office or Element.

13.2 Current MDL data are available in the QA Office.

13.3 Precision and accuracy data are available in the QA Office or Element.

## 14.0 POLLUTION PREVENTION

14.1 For information regarding the laboratory's pollution prevention policy and procedures, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

14.2 The quantity of chemicals purchased should be based on expected usage during its shelf life, space available for storage, and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratory operations, consult, "Less is Better: Laboratory Chemical Management to Waste Reduction" available from the American Chemical Society, Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington D.C., 20036.

## 15.0 WASTE MANAGEMENT

15.1 The Public Health Laboratory, in carrying out its mission, will do so in such a manner as to minimize pollution of the environment and manage its hazardous wastes in a safe and environmentally sound manner.

The Public Health Laboratory Division shall:

- Conserve natural resources through reduction, reclamation, recycling.
- Ensure that the Division meets all Federal, State, and Local regulations pertaining to hazardous waste disposal.
- Prevent pollution at the source whenever possible.

- Consider environmental impact when purchasing materials, handling chemicals and disposing of waste.
- Promote awareness and provide training opportunities for pollution prevention and hazardous waste management within the Division.
- Define the responsibilities of managers, supervisors and staff so that Division activities will be conducted appropriately and effectively with regard to waste management.
- Develop policies and procedures as needed to further these objectives.

15.2 For additional information regarding the laboratory's waste management policy, see the current version of the Public Health Laboratory Division Hazardous Waste Manual. http://fyi.health.state.mn.us/phl/safety/index.html

## 16.0 BIBLIOGRAPHY

16.1 Standard Methods for the Examination of Water and Wastewater. Method 4500-$S^{2-}$I and J. 21st Edition, On-line.

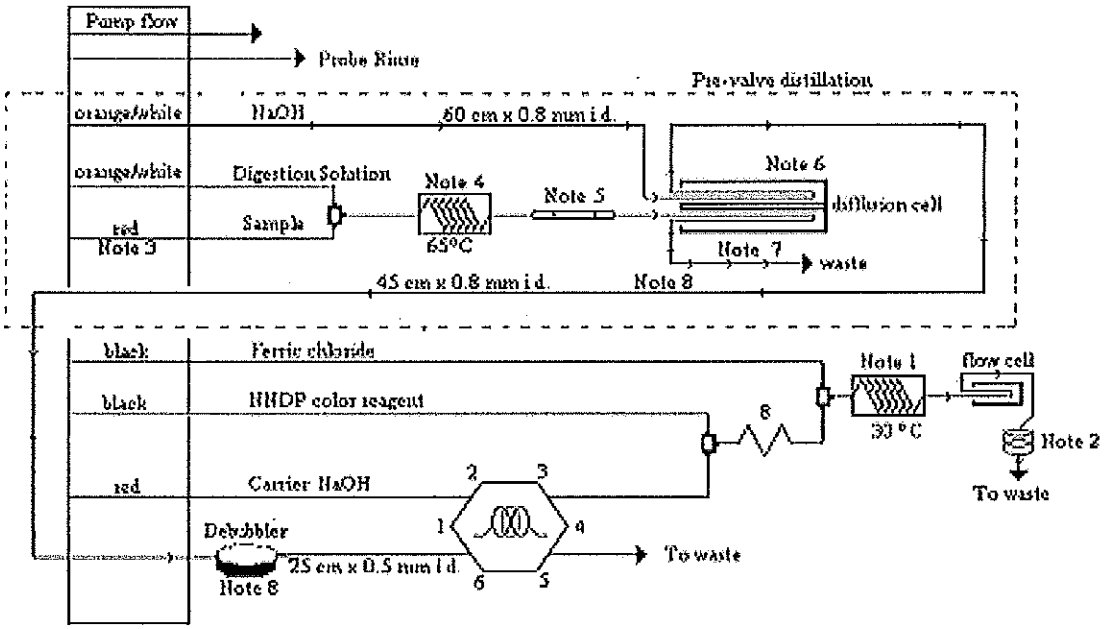
16.2 Lachat Instruments QuikChem® Method 10-116-29-3-A, Determination of Dissolved Sulfide by Flow Injection Analysis.

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

## 17.0 TABLES, FIGURES, VALIDATION DATA

17.1 The Initial Demonstration of Capability data are on file in the QA Office; the most current MDL, precision, and accuracy data are on file in the Environmental Laboratory.

17.2 Sulfide Manifold Diagram:




Carrier: 0.025 M NaOH (Reagent 5)
Manifold Tubing: 0.8 mm (0.032 in) i.d. This is 5.2 uL/cm.
AE Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.
QC8000 Sample Loop: 150 cm x 0.5 mm (0.022 in) i.d.

Interference Filter: 660 nm

Apparatus: An injection valve, a 10 mm path length flow cell, and a colorimetric detector module is required. The  shows tubing wrapped around the heater block at the specified temperature; see manifold notes for the length of tubing used.

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

Note: PVC PUMP TUBES MUST BE USED FOR THIS METHOD

Note 1: 650 cm x 0.8 mm i.d. tubing wrapped on the heater at 30°C

Note 2: 200 cm x 0.5 mm i.d. backpressure loop

Note 3: The sample line is replaced with a red/red pump tube. 45 cm x.0.8 mm i.d. is used to connect the sample line to the mixing tee which merges with phosphoric acid.

Note 4: 1200 cm x 0.8 mm i.d. wrapped on the 65°C heater. The lengths of tubing on the heater inlet and outlet are 53 cm.

Note 5: The 53 cm lead of tubing from the outlet of the 65°C heater is covered with 52 cm of high temperature sleeving, (1/16" i.d., Lachat Part No. 50364) for heat insulation and then connected to the diffusion cell inlet on the bottom half.

Note 6: Diffusion cell (Lachat Part No. 50332) is mounted on the manifold board. The Donor (bottom) and Acceptor (top) streams flow in the same direction.

Note 7: To the diffusion cell outlet, bottom half, connect 100 cm x 0.8 mm i.d. manifold tubing plus a waste line (Lachat Part No. 50932)

Note 8: The Debubbler is mounted on the manifold board near the valve. Replacement membranes are part number 85363. To install unit: Cut tubing with 2 nuts in half. Screw half into each port on the PEEK body. These are the inlet and outlet of the unit. If needed, 50 or 100 cm of 0.022" i.d. tubing can be added at the outlet of the debubbler connected to Port 6 of the valve.

Note 9: One O-ring is installed on each of the flares provided with the diffusion cell. Then attach the tan fitting, and then a union is attached to each of the flared tubing's.

17.3 Quik Chem® 8000

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

| | |
|---|---|
| Sample throughput: | 60 samples/hour, 60 seconds/sample |
| Pump speed: | 35 |
| Cycle speed: | 60 |

17.3.2 Analyte Data:

| | |
|---|---|
| Concentration Units: | mg/L of $NH_3$ N |
| Expected Inject to Peak Start: | 20 seconds |
| Expected Peak Base Width: | 49 seconds |
| Chemistry: | Direct |

17.3.3 Calibration Data:

| Level | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Concentration mg/L N | 5.00 | 2.50 | 1.00 | 0.50 | 0.10 | 0.05 | 0.0 |

| | |
|---|---|
| Calibration Fit Type: | 1st Order Polynomial |
| Calibration Rep. Handling: | Average |
| Weighting Method: | None |
| Force through Zero: | No |

17.3.4 Sampler Timing

| | |
|---|---|
| Min. Probe in Wash Period: | 5 seconds |
| Sample Period: | 24 seconds |

17.3.5 Valve Timing

| | |
|---|---|
| Load Period: | 15 seconds |
| Inject Period: | 45 seconds |
| Time to Valve: | 26 seconds |

Approved By: _____ Date: 7/3/2013
Jeffrey Brenner, Inorganic Unit Supervisor

Approved By: _____ Date: 7/3/2013
Paul Moyer, Environmental Lab Section Manager

Appendix I

**NPDES Equivalent Methods Do NOT Require Letter From USEPA**

Lachat Instruments has received many questions regarding USEPA Equivalent methods for NPDES reporting. Many customers have requested letters from the EPA stating these methods' acceptance. Lachat would like to stress that the USEPA will not be issuing letters for methods that fall within the flexibility allowed at 40 CFR Part 136.6 of the EPA's Method Update Rule (MUR), March 2007, and that these methods **are acceptable** for NPDES compliance monitoring. A good example of this is Lachat method 10-107-04-1-C. Lachat Applications submitted the method for review to the USEPA, requesting a letter stating that the method was acceptable for use in both NPDWR and NPDES compliance monitoring. The modifications in this method allow samples to be analyzed without pH adjustment due to the high flow rate of the buffer reagent, which allows the method to compensate for high or low pH samples. This method adjustment falls within the flexibility allowed at 40 CFR Part 136.6 of the MUR. Therefore, this method is acceptable for use in NPDES compliance monitoring and no letter is required (or will be issued) by the EPA.

The EPA states that, ***"The absence of a letter does not preclude use of Equivalent Lachat methods for NPDES compliance monitoring purposes."*** The modifications that fall within the allowed flexibility of the MUR do not require review as a Clean Water Act ATP.

The USEPA sent Lachat and all Regional ATP Coordinators this statement regarding this issue:

***"Due to increased inquiries on method flexibility we would like to stress:***

---

***Regions, States and permitting authorities should not expect a letter from the EPA's Office of Science and Technology (OST) stating that a modification that falls within the flexibility allowed under 40 CFR Part 136.6, which was added as part of the Methods Update Final Rule published in the Federal Register on March 12, 2007. Such modifications are acceptable for use in CWA monitoring. Letters for modified methods that fall within the scope of Part 136.6 will no longer be issued and the use of these methods are acceptable provided that they meet the performance requirements specified in the method.***

***Secondly, the flexibility allowed at Part 136.6 may be used to modify any method approved at Part 136 for compliance monitoring under the CWA including methods developed by VCSBs such as Standard Methods and ASTM International. If you choose to modify an approved method, in addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as Standard Methods, ASTM International or AOAC, International. This is further clarified in the attached memo from Richard Reding, Ph.D., Chief, EASB to Regional ATP Coordinators and Alternates titled: Citing Clean Water Act Limited-Use ATP Methods as Modifications dated April 14, 2008."***

Please contact the EPA or Lachat Instruments for copies of the above-mentioned EPA correspondence.

EPA Contacts for MUR questions are:

CWA ATP Coordinator Lemuel Walker (walker.lemuel@epa.gov)

The CWA methods Team (OSTCWAMethods@epa.gov)

Lachat would love to hear about your lab's experiences with the MUR. Is the intent to allow for more flexibility helping your lab? Please send Lachat any comments, good or bad, on the MUR to Lachat Technical Support (support@lachatinstruments.com).

## Appendix II

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF WATER

Date: April 14, 2008

To: Regional ATP Coordinators and Alternates

From: Richard Reding, Ph.D., Chief
Engineering and Analytical Support Branch
Engineering & Analysis Division, Office of Science & Technology

Topic: Citing Clean Water Act Limited-Use ATP Methods as Modifications

I am writing to our regional partners about citing a method for which a Region has issued a limited-use ATP approval letter that results in modifying another approved method. In addition to documenting that the modification works, to be fully transparent, the user also discloses that a Modified Method X, not just Method X, is being used. This annotation is especially important when modifying a method published by a standards organization, such as the Standard Methods Committee, AOAC, International, or ASTM, International.

For example, a lab with a CWA limited-use approval letter may conduct a luminescent measurement of dissolved oxygen (DO) with any approved method that requires a DO measurement, such as BOD or CBOD by SM5210B. However to do so, the lab will have a copy of a limited-use ATP approval letter. The lab SOP also will cite use of SM 5210B as "modified for luminescent measurement of DO in accordance with the limited-use ATP letter from the region" or similar wording.

Why do we recommend use of limited-use ATP approvals rather than wait for nation-wide approval? Because rulemaking can be a lengthy process. Thus in our national ATP letter, we recommend that regions consider approving use of the ATP under their limited-use ATP approval authority. Is it necessary for a limited-use ATP applicant to submit data, or do a side-by-side comparison in these cases? Our answer is generally no because methods that we review under the CWA ATP program already have multi-lab and comparability data.

Feel free to share this memo with your co-regulators, and the laboratory and method development community. Your contacts are the CWA ATP coordinator Lemuel Walker (walker.lemuel@epa.gov), or the CWA methods team (OSTCWAMethods@epa.gov).

cc: Lemuel Walker, CWA ATP coordinator
Steve Wendelken, SDWA ATP coordinator

Internet Address (URL) • http://www.epa.gov
Recycled/Recyclable • Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 25% Post-consumer)

# Appendix D: University of Minnesota Civil Engineering Laboratory QA Procedures and Standard Operating Procedures

# UMD Civil Engineering QA Procedures

## Quality Assurance / Quality Control (QA/QC) procedures for Johnson Research Group

N Johnson
Updated: 9/19/12

In order to ensure the quality of analytical data from a variety of techniques used to quantify chemicals in our lab, this document lays out procedures for how to ensure that the analytical equipment is giving consistent results and functioning as we expect for samples. These guidelines apply to:

- Anions and cations by Ion Chromatograph
- Ferrous iron by phenanthroline method
- Sulfide by ISE
- Sulfide by methylene blue spectrophotometric method
- Metals by ICP-MS
- Sulfate by turbidometric method
- pH & ORP by electrodes
- DOC on TOC analyzer
- Total elemental analysis on CHNS analyzer

The principle of QA/QC is to run checks with the instrument, at the beginning and periodically throughout the samples, to ensure that the instrument is functioning accurately and consistently and that there are no abnormal matrix effects that may compromise the analytical results. At least four or five types of QA/QC checks should be performed:

- **MB - Method Blanks (approx. every 10 samples)**
    - Water blank (usually DI water) with the exact composition of reagents as samples and calibration solutions and prepared using the same method (transfers, vials, dilutions, etc.) as samples; should be run more frequently (and after high concentration samples) if instrument carryover is experienced
- **OPR - Ongoing precision and recovery (approx. every 10 samples)**
    - A check of one of the calibration standards to make sure equipment is still performing as expected. For destructive analysis, if enough standard volume is prepared initially, this can be taken from the same bottle.
- **REF - Quality control sample, or reference material (min. once per batch)**
    - This is a sample of known concentration (typically analyzed by another lab) which can be used to check our own method against someone else's
- **DUP - Duplicates (min. once per batch, or every 20 samples)**
    - An exact replicate of one sample, prepared from the beginning in exactly the same way (not just back to a sample vial that was analyzed previously) to test method precision/reproducibility.
- **MET SPK - Method Spike (min. once per batch, or every 20 samples)**
    - This is typically performed for samples which require complex extraction procedure. A known amount of analyte is spiked into a blank matrix similar to the initial sample. This spike is then taken through all extraction/dilution/etc. steps and analyzed like a sample.
- **MS/MSD - Matrix Spike & duplicate (min. once per matrix)**
    - A sample which was analyzed alone should be split and prepared in exactly the same way. A known amount of analyte is then spiked into the duplicate sample. The original replicate will have a known amount of the analyte and can be subtracted from the spiked replicate to ensure recovery and or linearity of instrument response.

    - Many times a sample is split into three replicates and two are spiked to check precision/reproducibility and recovery at the same time.
- **Detection limit (once for the method)**
    - Established by analyzing many samples (>~7) at a concentration expected to be near the detection limit; the standard deviation of these analyses is used to establish a method detection that is known to be above zero with confidence according to a standard procedure.

**Typical analytical sequence**

As a result of the need for these quality assurance checks, a typical analytical sequence (for 30 samples) in a new matrix, might involve the following:

- An analytical blank
- Two to five non-zero calibration standards spanning the range of expected sample concentrations
- Ongoing Precision Recovery sample
- Quality Control or reference sample
- An analytical blank
- Seven samples
- A method blank
- Ongoing precision Recovery sample
- Three samples
- Duplicate sample(s)
- Four samples
- A method blank
- Matrix spike / matrix spike duplicate
- Five samples
- Ongoing Precision Recovery sample
- Four samples
- Method spike
- An analytical blank
- Seven samples
- Ongoing precision recovery
- An analytical blank

Although the above sequence involves 48 analytical runs for only 30 samples, the quality of the data will be much higher if these QA guidelines are followed and results can be reported with confidence.

A typical analytical sequence for a matrix that we have tested before and had reliable results for matrix spikes, could leave out matrix spikes. If OPR results consistently come out within 10% of expected values over a period of months of performing analysis, subsequent batches of samples (run on the same instrument) can proceed without a full calibration, but maintaining blanks and OPR checks.

# Sulfide

DOC316.53.01136

## USEPA[1] Methylene Blue Method[2] — Method 8131

### (5 to 800 µg/L)

**Scope and Application:** For testing total sulfides, $H_2S$, $HS^-$, and certain metal sulfides in groundwater, wastewater, brines and seawater.

[1] USEPA approved for reporting wastewater analysis. Procedure is equivalent to Standard Method 4500-$S^{2-}$ D.

[2] Adapted from *Standard Methods for the Examination of Water and Wastewater.*

## Test preparation

## How to use instrument-specific information

The *Instrument-specific information* table displays requirements that may vary between instruments. To use this table, select an instrument then read across to find the corresponding information required to perform this test.

**Table 393 Instrument-specific information**

| Instrument | Sample volume | Sample cell | Cell orientation |
|---|---|---|---|
| DR 6000 | 10 mL | 2495402 | Fill line faces right |
| DR 5000 | 10 mL | 2495402 | Fill line faces user |
| DR 3900 | 10 mL | 2495402 | Fill line faces user |
| DR 3800, DR 2800, DR 2700 | 10 mL | 2495402 | Fill line faces right |

**Before starting the test:**

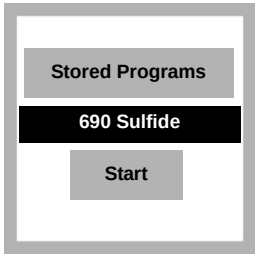
| |
|---|
| Analyze samples immediately. Do not preserve for later analysis. |
| Avoid excessive agitation of samples to minimize sulfide loss. |
| Some sulfide loss may occur if dilution is necessary. |
| Sulfide 2 reagent contains potassium dichromate. The final solution will contain hexavalent chromium (D007) at a concentration that is regulated as a hazardous waste by Federal RCRA. Refer to the current MSDS for safe handling and disposal instructions. |

**Collect the following items:**

| Description | Quantity |
|---|---|
| Sulfide 1 Reagent | 1–2 mL |
| Sulfide 2 Reagent | 1–2 mL |
| Water, deionized | 10–25 mL |
| Pipet, serological, 10-mL | 1 |
| Pipet Filler, safety bulb | 1 |
| Sample Cells (see *Instrument-specific information*) | 2 |
| Stoppers | 2 |

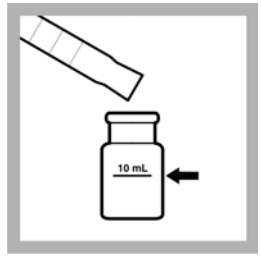
See *Consumables and replacement items* for reorder information.

## Methylene Blue Method

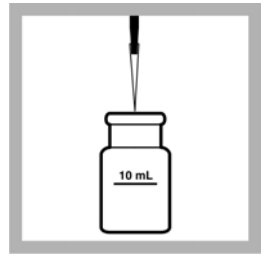



**1.** Select the test.

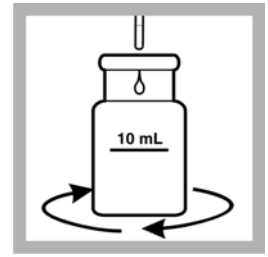
Insert an adapter if required (see *Instrument-specific information*). Refer to the user manual for orientation.




**2. Blank Preparation:** Measure 10 mL of deionized water in a sample cell.




**3. Prepared Sample:** Use a pipet to add 10 mL of sample to a second sample cell. Do not mix the sample more than necessary to prevent sulfide loss.




**4.** Use the dropper to add 0.5 mL Sulfide 1 Reagent to each cell.

Swirl to mix.


**5.** Use the dropper to add 0.5 mL Sulfide 2 Reagent to each cell.

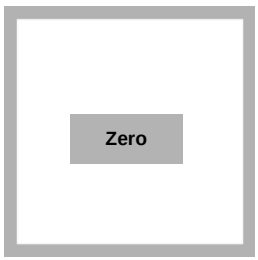

**6.** Cap or stopper the cell and immediately invert to mix.

The solution will turn pink initially and then turn blue if sulfide is present.


**7.** Start the instrument timer.

A five-minute reaction time will begin.

**8.** When the timer expires, wipe the blank and insert it in the cell holder.

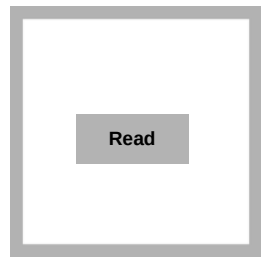



**9.** **ZERO** the instrument.

The display will show:

0.00 µg/L $S^{2-}$

**10.** Wipe the prepared sample and insert it in the cell holder.




**11.** **READ** the results in µg/L $S^{2-}$.

## Soluble sulfides

Complete the following steps to measure soluble sulfides.

1. Centrifuge a sample in completely filled, capped tubes.
2. Use the supernatant in place of the sample and follow the *Methylene Blue Method* procedure.

To estimate insoluble sulfides, subtract the soluble sulfide concentration from the total sulfide concentration.

## Interferences

**Table 394 Interfering substances**

| Interfering substance | Interference level |
|---|---|
| Strong reducing substances such as sulfite, thiosulfate and hydrosulfite. | Interfere by reducing the blue color or preventing its development. |
| Sulfide, high levels | High concentrations of sulfide may inhibit full color development and require sample dilution. Some sulfide loss may occur when the sample is diluted. |
| Turbidity | For turbid samples, prepare a sulfide-free blank as follows. Use this blank in place of the deionized water blank in the *Methylene Blue Method* test procedure.<br>1. Measure 25 mL of sample into a 50-mL Erlenmeyer flask.<br>2. Add bromine water by drops with constant swirling until a permanent yellow color just appears.<br>3. Add phenol solution by drops until the yellow color just disappears. Use this solution to replace the deionized water in step 2 of the procedure.<br>This pretreatment procedure removes sulfide from the sample, but the turbidity and any color will remain. The interference from turbidity or color will be corrected when the instrument is set to zero with this solution (step 9). |

## Sample collection, preservation and storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Prevent excessive shaking or prolonged exposure to air. Analyze samples immediately.

## Method performance

| Program | Instrument | Standard | Precision 95% Confidence Limits of Distribution | Sensitivity Concentration change per 0.010 Abs change |
|---|---|---|---|---|
| 690 | DR 5000 | 520 µg/L $S^{2-}$ | 504–536 µg/L $S^{2-}$ | 5µg/L $S^{2-}$ |

## Summary of method

Hydrogen sulfide and acid-soluble metal sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration. High sulfide levels in oil field waters may be determined after proper dilution. Test results are measured at 665 nm.

## Consumables and replacement items

### Required reagents

| Description | Quantity/Test | Unit | Catalog number |
|---|---|---|---|
| Sulfide Reagent Set, includes: | — | — | 2244500 |
| Sulfide 1 Reagent | 1 mL | 100 mL MDB | 181632 |
| Sulfide 2 Reagent | 1 mL | 100 mL MDB | 181732 |
| Water, deionized | 10 mL | 4 liters | 27256 |

### Required apparatus

| Description | Quantity | Unit | Catalog number |
|---|---|---|---|
| Pipet, serological, 10-mL | 1 | each | 53238 |
| Pipet Filler, safety bulb | 1 | each | 1465100 |
| Stopper, for 18-mm Tube | 2 | 6/pkg | 173106 |

### Optional reagents and apparatus

| Description | Unit | Catalog number |
|---|---|---|
| Bromine Water, 30 g/L | 29 mL | 221120 |
| Phenol Solution, 30 g/L | 29 mL | 211220 |
| Stopper, for 18-mm Tube | 25/pkg | 173125 |
| Flask, Erlenmeyer, 50 mL | each | 50541 |

**FOR TECHNICAL ASSISTANCE, PRICE INFORMATION AND ORDERING:**
In the U.S.A. – **Call toll-free 800-227-4224**
Outside the U.S.A. – **Contact the HACH office or distributor serving you.**
On the Worldwide Web – **www.hach.com**; E-mail – **techhelp@hach.com**

**HACH** COMPANY
WORLD HEADQUARTERS
Telephone: (970) 669-3050
FAX: (970) 669-2932

# Standard Operating Procedure for Analysis of sulfide by the methylene blue method (spectrophotometry)

Johnson Research Group
UMD-Civil Engineering
Updated 4/1/2013

The methods outlined in the Standard Methods for the Analysis of Water and Wastewater Method 4500 S2- D as implemented in Hach Sulfide method 8131 are followed on a Hach DR 2800 portable UV/VIS spectrophotometer.

Briefly, an appropriate volume of sulfide Reagent I (5%) is added to a clean sample vial to which sample is carefully delivered with a pipette. Sulfide reagent II is immediately (within 30s) added to the vial, capped, and gently mixed. Absorbance is read at 660nM within 30 minutes and compared to absorbance of blanks and standards. For low concentrations, blanks and standards are prepared in deoxygenated (but formerly oxidized) matrix water.

# Standard Operating Procedure for Analysis of anions by Ion Chromatograph

Johnson Research Group
UMD-Civil Engineering
Updated 4/1/2013

The methods outlined in EPA Method 300.1 are followed on a Dionex ICS-1100 Integrated IC system (AS-DV Autosampler).

Each sample is injected into the 25 μL sample loop, and separated using a Thermo Scientific AS22 IonPac 4x250 mm anion exchange column, after which each anion passes through the conductivity cell for detection. The eluent is 4.5 mM sodium carbonate and 1.4 mM sodium bicarbonate pumped at a rate of 1.2 mL min-1. The suppressor current is set at 31 nA and the column is continuously heated at 30º C.

In general (and especially when high sulfide is present), samples are filtered with 0.45uM polyethersulfone (PES) filter membranes and acidified to < pH 4.5 with concentrated HCl to convert all dissolved sulfide species (H2S , HS-, and S2-) to H2S, which reduces the amount of sulfide available to oxidize to sulfate prior to analysis. When chloride analysis is desired, the sample is split and analyzed separately for chloride. After acidification, samples are stored at 4C until analysis. Samples are diluted with Millipore water (18.2MΩ resistance) if necessary and placed in new 5 mL or 0.5mL Dionex polyvials with 20 μm-pore filter caps and loaded into the autosampler. If excessive iron has precipitated out of samples, they are re-filtered with 0.45 um PES filters.

A Thermo Scientific Anion Standard is used for preparing calibration standards, ongoing recovery checks, and matrix spikes.

# Standard Operating Procedure for Analysis of ferrous iron by the phenanthroline method (spectrophotometry)

Johnson Research Group
UMD-Civil Engineering
Updated 4/1/2013

The methods outlined in the Standard Methods for the Analysis of Water and Wastewater Method 4500 Fe- D are followed on a Hach DR 5000 UV/VIS spectrophotometer.

Briefly, an appropriate volume of reagents (HCl, Acetate buffer, Phenanthroline, DI water) are added to a clean sample vial to which sample is carefully delivered with a pipette. If concentrations are expected to be in excess of 200uM, a smaller sample volume is added and diluted to the expected sample volume with DI water.

The vial is then capped and gently mixed. Absorbance is read at 510nM within 30 minutes and compared to absorbance of blanks and standards. For low concentrations, blanks and standards are prepared in deoxygenated (but formerly oxidized) matrix water.

# UMD Civil Engineering Standard Operating Procedures

## Standard Operating Procedure for Hydrolab Sonde Calibration

Johnson Research Group
UMD-Civil Engineering
Updated 4/1/2013

Sonde calibration is to be conducted at the beginning of each use and the calibration status is to be checked whenever conditions change (e.g. going from the warm storage into the cooled storage rooms)

(a) Charge sonde overnight

The evening prior to use, remove the handheld part of the sonde and plug into the RS232 charger which is located in the case. The handheld unit needs to be turned **on** for charging to commence.

(b) Unplug the handheld from the charger and plug the sonde into the handheld using the same RS232 port on the back which the charger was plugged into.

(c) pH Calibration

- Rinse the probes with DI water
- Submerge the probes within the proper pH calibration fluid
- Press the "Setup/Cal" button on the handheld, then press "Calibrate" and press "Sonde" and wait for several seconds until the calibration menu appears.
- Navigate the menu on the handheld using the up and down arrow keys until "pH : Units" is highlighted and press the "Select" Button
- Enter the target pH of the calibration fluid by navigating with the left and right arrow keys to highlight different numbers. Press "Select" to enter that number within the new standard. Once the new standard value is entered, press "Done" and wait for several seconds.
- A message should come across the bottom of the handheld screen stating "Calibration successful" if this message does not display, or if the message reads "Calibration Failed" recheck the calibration fluid, make sure the standard was properly entered or obtain fresh calibration fluid.
- Repeat this process for calibration fluid at pH 4, 7 and 10

(d). Conductivity Calibration

- Thoroughly rinse the probes and plastic tubing with DI water.
- Make a Calibration solution using the solution within the sonde case. (2000 µS/cm)
    - e.g. Typical values of conductivity for the WD Wild rice/Sulfate Project_2013 fall between 300 and 500 µS/cm so a 400µS/cm calibration is appropriate. To make this, 50mL is required, mix 10 mL of the (2000µS/cm) solution from the case and combine it with 40 mL of DI water.
- Navigate to the "SpCond: µS/cm" item on the calibration menu.
- Using the left and right keys, enter the concentration of the calibration fluid that you made.
- Submerge the Sonde probes in the calibration fluid that you made, and press "Done" on the handheld device.
- A message should come across the bottom of the handheld screen stating "Calibration successful" if this message does not display, or if the message reads "Calibration Failed" recheck the calibration fluid, make sure the standard was properly entered or obtain fresh calibration fluid

(e). Dissolved Oxygen Calibration

- Rinse the probes and plastic tubing with DI water
- Fill the plastic case 1/3 full with DI water, replace the black plug, loosely screw the calibration tube into place on the end of the sonde, and turn the sonde upright (case down).\
    - The probes need not (and should not) be submerged during oxygen calibration
- Wait 5 min or until condensation begins to appear on the probes and tubing.
- Navigate to the "LDO%" on the sonde calibration menu and press "Select". Enter the current barometric pressure ( typically near 760 mmHg) and press "Done"
- "Calibration successful" should appear across the bottom of the screen on the handheld; if not, recheck the current barometric pressure and attempt to recalibrate; if the problem persists, contact Dr. Nathan Johnson for assistance.

NOTE: A simple method of submerging the probes of the sonde is to simply pour the calibration fluid into the clear plastic tubing and hold the sonde upside down (so the corded end of the sonde is facing the ground). By using this method, approximately 50 mL of fluid is required to submerge the probes (excluding turbidity) and perform the calibration.

# University of Minnesota Duluth – Civil Engineering

# Standard Operating Procedure for using ICP-MS (ELAN6000)

## Contents

## 1. A basic mindset

a. An appropriate mindset of using the Elan6000 ICP MS in the Research Instrumentation Laboratory of MWAH at UMD include

   i. Plan several days in advance and contact Bryan Bandli at MWAH 55 to ensure argon is present and equipment is functioning normally

   ii. Plan at least 2 hours to starting and warming up the ICP MS system.

   iii. Make a clear plan on how many samples to run and an estimation of the range of concentration of your samples (including dilutions if necessary).

## 2. Before turning on the system, here is the system checkup list

a. Power

   i. If the system has been used normally, the lab manager Bryan Bandli will maintain it powered and should be ready to use.

   ii. If the system is shut down, consult Bryan to power it up.

b. Argon

   i. Monitor the Argon pressure and be sure the tank is not empty, if the gage show less than one quarter of argon left, inform Bryan for new order. A full small tank of argon can last 8 hours and a big tank of argon can last about 40 hours for normal operation. However, the process of igniting plasma can consume extra amount of argon, especially when you have to try many times for ignition process.

   ii. Make sure the valves of argon flowing system are opened all the way. Check for green signs on " Instrument-front panel" on software interface.

c. Tubing

   i. Replace the tubing (the small one) of clamped by peristaltic pump with new tubing daily (or every 8 hours of running), remember to stretch it when you release the tubing from peristaltic pump. Replace the drain pump tubing (The large one) weekly.

   ii. Install sampling and draining tubing on peristaltic pump. Connect sampling tip to sampling tube, submerse sampling tip in Milli-Q water and turn on peristaltic pump, to make sure the flowing directions are correct and they drain (If needed, consult manual P4-13 for detail of reconnecting the Peristaltic Pump).

iii. Check and make sure the tubing at the back side of autosampler works well, otherwise replace it.

d. Cleaning skimmer cones and torch

i. Flip open the cover of main chamber, carefully slide the vacuum chamber and main interface to the left (Detail and pictures in Manual P5-14).

ii. Remove the two skimmer cones special special tool in the door (slide out for the first cone, and unscrew out for the second one).

iii. Clean the cones by immersing the tips only in soapy water and sonicating for 30 min.

iv. Rinse thoroughly with Milli-Q water and allow dry.

v. Reinstall cleaned, dry sampler and skimmer cones.

vi. Inspect torch and load coil for damage or contamination.

1. If torch has dirty spot, open the torch box, uninstall the torch, clean it by immersing it in 2% HNO3 for at least 3 hours (If the spot is not washed out, put it in 5% HNO3 or allow extra time) and rinse it with Milli-Q water. While a torch is being washing, ask Bryan for another one to use.

2. Reinstall the cleaned torch, make sure to use the black alignment tool to alight the torch according to the directions of the manual. There are two steps to alighn the torch, consult Manual P5-16-21 for detail. **This is a very important step**, the plasma will not turn on if the torch has not been well alighted and installed.

vii. Slide back the vacuum chamber and main interface to position, be sure to hear the 'click' sound for locking, cover back the main chamber.

e. Tuning solution

i. Be sure to have unexpired tuning solution and Milli-Q water ready and handy when the system is warming up.

f. Check the washing solution and waste tank

i. Make sure there is enough washing solution (2% HNO3) in the tank, refill as needed.

ii. Make sure the tubing connects the washing solution and peristaltic pump is working well,

1. Make sure the end of the hose inserted in washing tank is submersed in the solution.

2. Be sure to pump that pumping washing solution is working well. This pump is located at the back of the auto sampler. Check the rubber tubes clamped at in the pump, replace it if you see any damage. This pump only operates when the autosampler is used.

iii. Make sure the tank containing waste solution has enough space to receive waste during your sample run, empty it as needed (Ask Bryan for help).

iv. Both tanks containing washing solution and waste are sitting on the floor, underneath the auto sampler.

## 3. Turning on Plasma

a. Submerse sampling tip in Milli-Q water, check it occasionally when system is warming up, refill Milli-Q as needed.

b. Double click to start the ELAN6000 software and enter the service mode using password ”Elan6000” (Options/Enter service Mode).

c. Click on the “Devices” / “Peristaltic pump” / “Connect” buttons to connect the system to peristaltic pump.

   i. Start the pump with rotating counterclockwise at 24 rpm by clicking the button showing right direction.

   ii. Double check the flowing direction and make sure the tubes drain.

d. Click on the “Instrument” button.

   i. Ensure the instrument is ready (No part of the system model indicates red on the front panel!)

   ii. Start the plasma ignition sequence by clicking the ‘start plasma’ button or pressing the green button on interface of Elan6000.

e. Switch to the Service tab and click “plasma” tab located at the bottom of the interface.

f. Closely watch the plate voltage and when it jumps to 3899 V (this takes about 60 s from the time the “start” button is pressed) press the grill ignitor button.

   i. If everything works well, the plasma will pup on when the igniter button is clicked and you can see the bright blue plasma from the viewing window;

ii. If the plasma is not on, wait till this ignition sequence end by observing the values on 'plasma' tab turn back to normal (this process normally takes about 1-2 minutes), switch back to front panel tab and check everything is green.

iii. Repeat steps d – f to ignite the plasma, if fail more than 5 times, consult Bryan for help. If Bryan is not here, run trouble shutting according to manual P6-3.

g. Once the plasma is started, allow the instrument to warm up for 30-45 min. I normal use this time to prepare for standard solutions.

## 4. Optimizing and Tuning the system

a. After system warm up, place the end of the sampling tube into the tuning solution. (Don't put the sampling tip into the whole bottle of tuning solution as it will contaminate it, but to pour some out into a second container, such as a 50 ml centrifuge tube, and put sampling tip in it)

b. X-y alignment. The target of this step is to find the strongest signal that the system can produce by alighting the position of sampling introducing system, the torch and coil, with the sampling receiving system, the skimming cones.

i. On main menu of ELAN6000 software, click 'file', 'Open workspace', select 'x-y.wrk' and 'open'.

ii. In sample tab, click 'analyze sample' or 'analyze blank'

iii. Switch to 'real time' tab, select 'signal' in the box from the dropdown menu.

iv. Watch the change of the signals.

v. Flip open the main chamber cover, adjust the X and Y spectrometer alignment knobs located right outside of the torch box (adjust the rear knob first) to maximize the signal.

vi. If the maximizing process has not been completed by one run of 'analyze sample/blank', repeat steps 5b i-v to complete the process.

vii. Cover back the main chamber.

c. Tune the system. The purpose of this step is to tune and optimize the instrument by automatically run a series of selected procedures.

i. Click on the "SmartTune" button on main interface of software.

ii. Click 'file' and 'open', select the desired tuning files from the list of pop-up window.

1. If the ICPMS has not been used for some days, I use the full tuning procedure by selecting “smart tune full UMD.swz” file; if the system has been used normally (daily), it is not necessary to run the full tune procedure, I run ‘smart tune daily’ for saving some time and tuning solution, watch and be sure the centrifuge tube containing tuning solution is not empty while the tuning procedure is running, refill if needed.

2. You can (normally don’t need to) select and edit the optimization procedures by clicking the ‘edit list’ button at the left hand side of the window and choose the way and procedures to run for tuning. But for the beginning, I will just run the ‘Smart tune daily’ file, or ‘Smart tune full UMD’ file.

3. On the right hand side of the window, select the right number of position of the sampler at which you put your tuning solution, or select the choice of ‘Use manual sampling (without autosampler)’, no need to worry about right setting of the position of the tuning solution in auto sampler.

    a. Using auto sampler allowing automatic run of the tuning procedures, no need to interfere the system during the process and you can use this time to work on your standard solution and preparation of samples. But still need to click and save the results of daily performance check before the system can automatically run the rest of the procedures. Some tuning procedures scheduled ‘daily performance check’ at the beginning and the end, be sure to check and save the results of this step, since the tuning procedure will not continue until you save the daily check result.

    b. By selecting ‘Use manual sampling (without autosampler)’, you don’t need to worry about where to put your tunning solution, you can put it anywhere, but it requires active interaction with the system during the tuning procedure, by clicking ‘OKs’ after each tuning step.

iii. Click the ‘optimize’ button ( the one on the smarttune window, not the button on the main menu) and wait for the system to complete the optimization.

1. The results of the tuning procedure is stored and can be viewed at the default optimization file which is used in the process of running the sample later on.

2. The result of daily performance check is reported as a picture file and required timely save, we save them in 'My document/Daily performance report', put the date at the end of the report before saving your report so you can keep track of them later.

3. The results of smart tune, especially the process of the 'AutoLen', may not pass and the daily performance check may indicate fail if the default parameters are used for the tuning procedure. It is said that the default setting set by the manufacturer was pretty strict and after several years of running the system may not meet the criteria. Making sure the X-Y alignment has been done well and the system is running OK, It is OK to adjust the parameter to an acceptable level, or accept the results with a little bit lower performance(Judge this by consulting the software manual and comparing your performance check result with the past performance check results stored it the computer and recorded in the log book.)

iv. Once the optimization is complete, record the results of daily performance check and save a copy of the report to the "Optimization records" folder in My Documents.

## 5. Defining Method files (Consult ElAN6000 Software Guide P47 - 62)

a. A method file has to be pre-defined before any sample can be analyzed. A sample file should be defined based on the target elements of your samples. There are defined quantitative method files, such as 'quantitative analysis_Johnson_LowConc.mth', stored in the computer, which include analytes of of Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr. Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, PB, Sr, Ti, Zn. I use 'quantitative analysis_Johnson_LowConc.mth' for low concentration (0.3ppb to 100 ppb) and 'quantitative analysis_Johnson' for high concentration (40ppb – 5000bbp) analysis.

b. Switch to Method window by clicking 'Method' tab

i. Time Tab

1. Make sure your target elements are included it the list of the analytes, also of course, they should be included in your standard solution.

2. The factors of 'Sweeping/reading time', 'Reading/Replicating', and 'Replicate' are changeable, the selection of 40, 1, and 3 respectively for the three parameters are reasonable and working well in past measurement. Change of these selections affect the volume of the sample needed for the measurement.

ii. Processing Tab

1. Define how the instrument should detect and process the elements in the samples. The selection in the previous method files worked well. They are changeable as needed.

iii. Equation Tab

1. List the same element you selected in the Time tab. Here you can select different isotopes of each element or use equation for reducing interference in the process of measurement.

iv. Calibration Tab (This **is important for setting up your file**)

1. In this window you need to define the concentrations of each elements in your standard solution.

2. This information is used by the system to automatically calculate the results of your sample.

3. Make sure the list of analytes and their Mass numbers in calibration window are the same as they are in the Processing and Time Tabs.

4. Double check and make sure sample unit and calibration unit are consistent for each element.

v. Sampling Tab

1. Here to define the criteria of sampling process, such as the time for sample flush, read delay, washing time. If you see any contamination between samples from the results of your measurement, you can come back here to adjust the time of washing and speed of the pump.

vi. Report Tab

1. This Tab located at the right hand side of the method window.

2. On report view, you can define the template of report for measurement results. I defined and use two template files,' Johnson report.rop' and 'Johnson report_simple.rop', you are welcome to use or to adjust them. Don't check 'sent to Printer' or 'Generate NetCDF file'.

**3.** On Report to file, check 'report to file', select the right report template file in the box of 'Report options template', define the report file name, otherwise the results of a new run or reprocess will overwrite the report file that you have defined before and you will lose the previous results if you select overwrite the result under 'file write option'.

4. If you select the 'Append' under the 'file write option' , you will have new results append at the end of previous defined file, resulting a long files, but maybe useful if you split a batch of sample into several parts and run in different times.

5. Under report format, select all options of 'use titles', 'use delimiter', and 'use separator', they are important for viewing the result later in Excel.

## 6. Defining sample file

a. A sample file has to be defined before a sample, or a batch of samples can be analyzed.

b. Switch to Sample Tab by clicking Sample on main menu.

   i. Select 'batch' tab unless you are to measure only one or two samples or bear to switch the sampling tip every 4 minutes for a batch of samples.

   ii. Under 'Batch', put all of your standard solutions, samples, spike samples, replicates in auto sampler.

   iii. Clearly label and define the sample IDs and record the location (A/S Loc., this information will be detailed in the following 'auto sampler' section) for each sample, fill this information in the sampling table, or you can use sample template to build the sample file.

   iv. In column of measuring action, I select 'run sample' for all samples listed under A/S Loc., including blanks, standard solutions, spikes, and replicates, for the analyze process, then to define calibration standards and blanks when I come back to reprocess the data after a run has completed. I tried to define the blanks and calibration solutions beforehand the analysis process, it turned out repeat running the sample three times and need to use three times of the sample volume of a single run, and the results were confusing to me as well. The process of one time run and reprocess at the end seemed work and plain to me, so I prefer to use this method.

   v. In Method column, select your predefined method file. Fill down and copy to each sample, unless you are intend to use different method for various samples.

   vi. In Sample Type column, I select 'sample' for each sample, unless you want to use auto QC/QA function, you may want to select various sample type, i.e., QC spike, QC dilution etc. to have the system automatically calculate QC for you, but then you need to enable QC function when you define your method file. I have not tried that.

   vii. Information in columns of Aliquot volume and Dilution to Volume are very useful when you have to dilute your samples. I found it very helpful when I

reprocess my data as these values are always there, and in the report of results this function save me quite some time in calculating back the original concentration of the samples. So use it with care as needed.

viii. On the upper part of the sampling window, click button of 'Summary', you can define a file receiving a summary report of each reprocessing of the data.

c. Auto Sampler

i. Autosampler is important part for running a batch of sample.

ii. Switch to device tab by clicking 'Device' on main menu.

iii. Switch to autosampler tab

iv. Select autosampler 'Cetac ASX-500', Tray name 'ceasx500\as500d.try'.

v. Select Port 'GPB1'

vi. Initialize the sampler by clicking 'Initialize'

vii. Numbering the location of the sampler

1. The first row on the top fit for 50 ml centrifuge tube is numbered as one to ten, from left to right. Standard solutions are used to put in these locations.

2. There are four sampling trays sitting on the floor of the auto sampler, each tray holds 24 sample tubes (3 columns and 8 rows), from left to right, the sample tubes located at the first tray are numbered as 11 to 18 for the first column, 19 to 26 for the second column, 27 to 34 for the third column; in the second tray, from left to right, the first column is number as 35 to 42, the second column is number as 43 to 50, and so on. Total 106 samples (including standard solutions) can be put in the auto sampler at the same time. The table below shows the setup of the tray in auto sampler.

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| 11 | 19 | 27 | 35 | 43 | 51 | 59 | 67 | 75 | 83 | 91 | 99 |
| 12 | 20 | 28 | 36 | 44 | 52 | 60 | 68 | 76 | 84 | 92 | 100 |
| 13 | 21 | 29 | 37 | 45 | 53 | 61 | 69 | 77 | 85 | 93 | 101 |
| 14 | 22 | 30 | 38 | 46 | 54 | 62 | 70 | 78 | 86 | 94 | 102 |
| 15 | 23 | 31 | 39 | 47 | 55 | 63 | 71 | 79 | 87 | 95 | 103 |
| 16 | 24 | 32 | 40 | 48 | 56 | 64 | 72 | 80 | 88 | 96 | 104 |
| 17 | 25 | 33 | 41 | 49 | 57 | 65 | 73 | 81 | 89 | 97 | 105 |
| 18 | 26 | 34 | 42 | 50 | 58 | 66 | 74 | 82 | 90 | 98 | 106 |

d. After defining sampling file, putting samples in the appropriate location in the auto sampler, and initializing the auto sampler, you can click the button of 'Analyze Batch' in sampling window. The batch of samples will be analyzed automatically.

e. You can also use schedule function by click 'schedule' on main menu, to define and schedule auto analysis, wash, and shutdown procedures. So you can be sure the plasma will be shut down after the bath measurement is done. However, it is crucial for occasional check and to be sure the sequences are running appropriately when one or more batches of measurement are scheduled. If a response to the system is asked for by the software during a run, the system will stop the analyzing process until the respond has been received, while the pumps and plasma are still running.

## 7. Shutdown

a. At the end of sample runs, place the end of the sample pump tubing in milli-Q water and allow to run for 10 min.

b. Stop the plasma by clicking on the stop button in the plasma section of the instrument front panel window. The instrument will go through an internal shutdown procedure and continue making noises for about a minute.

c. Stop the peristaltic pump.

d. Release the pump clamps and remove the pump tubing.

e. Open the cover of the auto sampler to allow the acid gas to release.

## 8. Preparing standard solutions and samples

a. Standard solution

   i. Never insert a pipette tip directly into the bottle containing original stock solution, always use a second contained to hold a small amount of stock solution and work with it.

   ii. Standard calibration need to be made every day. Typically when you restart the plasma and retune the system, you need a new standard calibration for a new run.

   iii. Use 2% HNO3 to dilute the stock and make standard solution. As a stock solution contains multiple elements that are of interest in your sample, multiple calibrations for different elements can be create at the same time, given that the appropriate concentration settings in each step of standards for each element is well defined. Table 1 and 2 below are examples to prepare calibration solutions, for both low and high concentrations.

iv. The target concentrations of the elements in each standard solution were calculated based on one specific element, e.g., concentration of Ag is used as base in this example to calculate concentrations for other elements. I set up a spreadsheet to quickly calculate the corresponding element concentrations for each level of standard solution. This information is necessary to fill in the Method file.

v. A spreadsheet is also helpful on calculating the volume of stock solution and 2% HNO3 for making standard solutions. Table 3 and 4 are examples for it. The calculation is based on the concentration of Ca.

Table 1. Example of standard concentration for multiple elements (High concentration).

| Elements | Target Concentration, ppb | | | | | | |
|---|---|---|---|---|---|---|---|
| | Original Stock | Std 1 | std 2 | std 3 | std 4 | std 5 | std 6 |
| Ca | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Mg | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Na | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Fe | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| K | 100000 | 400 | 1000 | 3000 | 7500 | 17000 | 50000 |
| Mn | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Mo | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Ag | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Al | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| B | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Ba | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Bi | 100000 | 400 | 1000 | 3000 | 7500 | 17000 | 50000 |
| Cd | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Co | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Cr | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Cu | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Li | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Ni | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Pb | 100000 | 400 | 1000 | 3000 | 7500 | 17000 | 50000 |
| Sr. | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |
| Ti | 50000 | 200 | 500 | 1500 | 3750 | 8500 | 25000 |
| Zn | 10000 | 40 | 100 | 300 | 750 | 1700 | 5000 |

Table 2. Example of standard concentration for multiple elements (Low concentration).

| **Elements** | **Target Concentration, ppb** | | | | | | |
|---|---|---|---|---|---|---|---|
| | **Original Stock** | **Std 1** | **std 2** | **std 3** | **std 4** | **std 5** | **std 6** |
| Ca | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Mg | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Na | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Fe | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| K | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Mn | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Mo | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Ag | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Al | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| B | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Ba | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Bi | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Cd | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Co | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Cr | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Cu | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Li | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Ni | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Pb | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sr. | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Ti | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |
| Zn | 20000 | 0.3 | 1 | 3 | 10 | 30 | 100 |

Table 3. Example of calculation for needed volumes of stock and 2% HNO3 for preparing calibration solutions.

| Standards | Target conc., ppb | Volume of final solution, ml | Stock conc. ppb | Volume of stock solution needed, ul |
|---|---|---|---|---|
| Std1 | 40 | 10 | 10000 | 40 |
| std2 | 100 | 10 | 10000 | 100 |
| Std3 | 300 | 10 | 10000 | 300 |
| Std4 | 750 | 10 | 10000 | 750 |
| Std5 | 1700 | 10 | 10000 | 1700 |
| Std6 | 5000 | 10 | 10000 | 5000 |

Table 4. Example of calculation for needed volumes of stock and 2% HNO3 for preparing calibration solutions.

| Standards | Target conc., ppb | Volume of final solution, ml | Stock conc. ppb | Volume of stock solution needed, ul |
|---|---|---|---|---|
| Std1 | 0.3 | 10 | 10 | 300 |
| std2 | 1 | 10 | 100 | 100 |
| Std3 | 3 | 10 | 100 | 300 |
| Std4 | 10 | 10 | 100 | 1000 |
| Std5 | 30 | 10 | 100 | 3000 |
| Std6 | 100 | 10 | 20000 | 50 |

b. Samples

   i. All samples to analyze metal concentrations are needed to preserve with 2%-5% HNO3. Since we are using 2% HNO3 for washing solution and for preparing calibration standards, we should be consistently using 2% HNO3 to preserve and dilute samples.

   ii. If your original samples have not been preserved with 2% HNO3, i.e., your solution is not containing 2% HNO3, the concentration of HNO3 in your samples (diluted) are necessary to be adjusted to 2% HNO3 using 100% HNO3. The amount of 100% HNO3 needed to add to samples is calculated based on the final volume of your sample and the content of HNO3 originally contained in your sample.

   iii. To be sure a smooth analysis process, put no less than 3 ml of each sample in vials that are set in trays of auto sampler. If you need replicate from the same vial, consider to double the sample volume.

## 9. Data processing

a. After running a batch of sample, with the plasma shut down, the data can be processed and reprocessed.

b. Go to 'Dataset' tab on main menu, from the list of the analyzed samples; select the ones you are to process.

c. In the column of 'Read type', define the selected samples as blank, sample, standard, spike, etc. by right click and make appropriate selection on the pop out window.

d. Double check the columns of 'Aliquot Volume' and 'Dilute to Volume' for each selected sample, correct it if necessary. This can save you quite some time in reporting the results.

e. Click the button of 'Summary Report' to set up a file to receive a summary result of your processing.

f. Check 'Use original Conditions' if nothing change from the original conditions, e.g. aliquot volume, method file, etc.. Uncheck this option if you made any change from the original condition for this reprocess.

g. Check 'Save Reprocessed Data' if you want to save a copy of the reprocessed data which is useful for you to view back how and which reprocess have been done, otherwise, leave it there.

h. The data can be reprocessed many times with various conditions. If you want to save a report of the results differ from the report generated from previous reprocess, go to

'Method' tab and click the 'Report', and defile a different name. otherwise, the new results will overwrite or append at the end of the old one, depending on the selection you have made before in 'Report' tab.

i. Click 'Reprocess' data, the software will reprocess your data.

j. Save your new standard calibration with a new name with current date if you just have done a calibration by assigning the standard solutions. This new calibration will be used to calculate the actually concentration of the samples that you will be reprocessing.

k. Be sure the currently opened method file is the same as the method file that you have defined on the 'Method file' column on 'dataset' window, corresponding to the data that you are to reprocess. The system read the method file that is currently open as the method to reprocess you data, if your opened method file is no consistent with the method file you are suppose to use for reprocessing the data, the results will be confusing.

## 10. Viewing the result reports

a. The result report can be viewed and converted to Excel file.

b. In Excel, click 'Open', look in C:\Elandata\ReportOutput, select your result file, 'Open'.

c. In Text Import Wizard, select 'Delimited', 'Next'; in step 2, select 'Tab','Space', and 'Comma'; 'Next', and 'Finish'.

d. From the report, you can see the detail information based on options that you have defined in the report template. If desired, You can change the template and reprocess the data for other forms of results.

e. For a short and quick report that only shows the resulted cpt for each sample, open the summary report you just defined before reprocess process.

f. Once you open your text report file in Excel, save it as Excel file so that it can be easily open next time.

# Appendix E: National Lacustrine Core Facility/ Limnological Research Center Laboratory QA Procedures and Standard Operating Procedures

**STANDARD OPERATING PROCEDURE: TOTAL CARBON/TOTAL NITROGEN (TC/TN)**

**Preparation and analysis of MN lake sediments submitted to the LLO for TC/TN analysis**

Sample condition –

Samples were received from the LRC freeze-dried and ground (Myrbo) in snap-top plastic containers. Some samples contained visible vegetative material. Some samples contained small pebble sized material. Inhomogeneity may result in greater analytical variability or misleading results.

Preparation –

Samples were mixed with a metal spatula before subsampling. Milligram quantities of sample were packed into tin capsules and weighed on a microbalance. Sample FS-63 Caribou was not stable weight-wise. The entire sample was placed in a 60°C oven for 3 hours and cooled in a desiccator before subsampling.

Instrumentation, Analysis and Quality Assurance –

Acetanilide was used as a calibration standard and as a quality assurance sample. A MN Lake Sediment sample prepared in duplicate and a QA sample were run at least every tenth sample. All QA samples were within ±5% of the known Carbon/Nitrogen weight percent for that material.

Elemental analysis was performed using a Costech 4010 ECS.

Paraphrasing from Costech literature: At the start of an analytical cycle, helium carrier gas was switched to a volume of oxygen. Samples were dropped sequentially into a combustion reactor at 1020°C prior to the arrival of oxygen. The sample and tin capsule reacted with oxygen and combusted at 1700-1800°C. The sample was broken down into elemental components, $N_2$, $CO_2$, and $H_2O$. High performance copper wires at 700°C absorbed excess oxygen not used for sample combustion. The gases flowed through a water trap and then through a gas chromatography (GC) separation column at 35°C. As the gases passed through the GC column, they were separated and detected sequentially by a thermal conductivity detector (TCD). The TCD generated a signal proportional to the amount of element in the sample. Costech EAS software compared the elemental peak to a known standard material (after calibration) and generated a report for each element on a weight basis.

Each sample chromatogram was visually inspected. Manual integration was performed as necessary to use only the area of the element of interest in calculations.

Results were manually transferred to the spreadsheet provided by Amy Myrbo and reported via email.

**STANDARD OPERATING PROCEDURE: TOTAL SULFUR (TS)**

**Purpose and Analysis Overview (after S. Grosshuesch)**

The analysis of total sulfur is accomplished by combustion using two furnaces aligned in sequence. A sample is weighed into a ceramic combustion boat and covered with $V_2O_5$. The boat is pushed inside the first furnace where sample ignition occurs at 1050°C. In the presence of $O_2$, sulfur is converted to $SO_2$ and SO. These gas products are carried through to the second furnace, set at 825°C, where they react with a mixture of granular copper oxide and reduced copper filings to ensure that all sulfur is converted to $SO_2$. The $SO_2$ is purged into the sulfur coulometer cell, where it is absorbed and titrated.

The coulometer titration cell contains an anode and cathode compartment. The anode compartment contains platinum-detector and -generating electrodes. The cathode compartment contains a single platinum cathode. The anode compartment is filled with a solution containing methanol, pyridine, water, and tetrabutylammonium iodide; the cathode cell compartment contains a phosphoric acid solution. Inert carrier gas ($N_2$), containing sample sulfur as $SO_2$ or $H_2S$, is delivered to the anode cell compartment. Free iodine is electrochemically produced in the anode cell and reacts with the sulfur gas, as illustrated in the following reactions:

Anode reactions: $SO_2 + I_2 + 2H_2O \leftrightarrow H_2SO_4 + 2I^- + 2H^+$
$H_2S + I_2 \leftrightarrow 2H^+ + 2I^- + S0$
$2I^- \leftrightarrow I_2 + 2e^-$

Cathode reaction: $2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$

The decrease in free iodine proportionally decreases the sulfur detector current, automatically activating the titration current and generating $I_2$ stoichiometrically. Hydrogen gas is produced in the cathode cell at a rate equivalent to that of iodine generation. After the majority of the analyte is titrated, an increase in the detector current and free $I_2$ occurs, ultimately stopping the titration when the initial iodine concentration is reached. The titration current is continuously monitored, integrated, and used to calculate the quantity of sulfur delivered to the anode cell. The significant advantage associated with the coulometric titration of sulfur is that the current is the titrant and as a result there is no need for generating and applying standard calibration curves. Most sample analyses for total sulfur can be completed within 10 min. Longer analysis times result if the sample contains more than about 3000 μg of sulfur or if sulfur-bearing compounds in the sample resist oxidation. Analysis times for AVS and CRS measurements are highly dependent on the sample type and reactivity of reduced sulfur compounds present in the sample. (AVS= acid volatile sulfur, CRS= chromium reducible sulfur)

Safety

The following section regards sound laboratory techniques, safety practices, and manners. You are responsible for following these procedures. The chemicals, glassware, and equipment are potentially hazardous. Lab staff must specifically train you before beginning the procedure. Required personal protective gear: gloves and safety glasses must be worn at all times. You must wear closed toe shoes and long pants. If you have long hair, make sure to tie it back. If you are found without any of these required personal safety devices you will relieved of duties. All sample prep work that involves vanadium penoxide should be conducted in a fume hood while wearing a lab coat, goggles, and nitrile gloves.

**Anode Solution (30% Pyridine):**

*Acute and Chronic Effects:* **POISON** Irritation to contact area, drowsiness, headache, unconsciousness, anorexia, fatigue, muscle cramps or incoordination, nausea, vomiting, dizziness, diarrhea, sweating, CNS depression, impaired vision, blindness, difficult breathing, cardiac depression, liver and kidney damage, dermatitis.

- Inhalation: Irritant/narcotic
- Skin Absorption: Irritant/sensitizer/narcotic
- Eye Contact: Irritant
- Ingestion: Narcotic/toxic
- Signs and Symptoms of Exposure: Nasal and throat irritation with unpleasant taste in mouth. Diziness, drowsiness, and headaches
- Medical Conditions Aggravated by exposure: Liver, kidney, or central nervous system disorders

*Compound Specific PPE:* Wear nitrile gloves, safety goggles or face mask, and lab coat when pouring anode solution in calibration cell. While coulometer being used vent coulometer anode half-cell to fume hood.

*Storage:* Store in tightly closed container, away from heat or flame. Storage area should be well ventilated. Store away from oxidizers, strong acids, and perchlorates.

*Disposal:* Dispose of by means in compliance with all State, Local, and Federal Regulations

**Cathode Solution (Phosphoric Acid):**

- Inhalation: Corrosive, causes irritation with coughing, choking and burns of mucous membranes. Symptoms include dizziness, headache, nausea, weakness and pulmonary edema. Repeated exposure can cause inflammation and ulcerative changes in the mouth and bronchial pneumonia

- Skin Absorption: Corrosive, causes pain or burns. Repeated exposure may cause dermatitis. Studies show that skin adsorption may occur.

- Eye Contact: Eye burns, pain, lacrimation, photophobia from corrosiveness. Injury ranges from irritation to conjunctivitis to blindness, depending on the concentration and duration of exposure.

- Ingestion: Corrosive, causes burns of mucous membranes of the mouth, throat, and esophagus. Symptoms range from inflammation of respiratory distress to death, depending on the concentration and duration of exposure. Symptoms may be immediate or delayed

- Signs and Symptoms of Exposure: Any irritation or burning of the eyes, skin, or respiratory system, or violent gastroenteritis.

- Medical Conditions Aggravated by exposure: Pre-existing skin disease or respiratory disorder.

*Compound Specific PPE:* Wear nitrile gloves, safety goggles or face mask, and lab coat when pouring anode solution in calibration cell.

*Storage:* Store in tightly closed container, away from heat or flame. Storage area should be well ventilated. Store away from strong bases.

*Disposal:* Dispose of by means in compliance with all State, Local, and Federal Regulations

**Methanol:**

*Acute Effects:* Hazardous in case of skin contacts: irritant if ingested, inhaled, or if in contact with eyes. Slightly hazardous in case of skin contact (permeator). Severe over-exposure can result in death.

*Chronic Effects:* Prolonged contact with skin can cause dermatitis or aggravate existing skin problems. Methanol is readily absorbed into the body following inhalation and ingestion. Skin absorption may occur if the skin is broken or exposure is prolonged. Once absorbed, methanol is rapidly distributed to body tissues.

*Compound Specific PPE:* All sample prep work that involves methanol should be conducted in a fume hood while wearing a lab coat, goggles, and nitrile gloves.

*Storage:* Store in a segregated and approved area. Keep container in a cool, well-ventilated area. Keep container tightly closed and sealed until ready for use. Avoid all possible sources of ignition (spark or flame).

*Small Spill:* Dilute with water and mop up, or absorb with an inert dry material and place in an appropriate waste disposal container.

*Large Spill*: Flammable and poisonous liquid. Keep away from heat or sources of ignition. Adsorb with dry earth, sand, or other non-combustible material. Call for assistance with disposal.
*Disposal:* Dispose of by means in compliance with all State, Local, and Federal Regulations

**Vanadium Pentoxide:**

*Acute Effects:* Very hazardous in case of ingestion or inhalation. Hazardous in case of skin contact (irritant) or eye contact (irritant). Slightly hazardous in case of skin contact.

*Chronic Effects:* The substance may be toxic to gastrointestinal tract, upper respiratory tract, and skin. Repeated or prolonged exposure to the substance can produce target organ damage. Repeated exposure to highly toxic material may produce general deterioration of health by an accumulation in one or many human organs.

*Compound Specific PPE:* All sample prep work that involves vanadium penoxide should be conducted in a fume hood while wearing a lab coat, face mask, goggles, and nitrile gloves.

*Storage:* Store in a tightly closed container. Store in a cool, dry, well-ventilated area way from incompatible substances.

*Small Spill:* Use appropriate tools to put the spilled solid in a convenient waste disposal container.

*Large Spill*: Poisonous solid. Do not touch spilled material. Prevent entry into sewers, basements, or confined areas. Call for assistance for disposal.

*Disposal:* Dispose of by means in compliance with all State, Local, and Federal Regulations

*Exposure Limits:* 0.1 mg/m3 from OSHA (respirable)

Record Keeping

1. Make sure to record the date, number of blanks, number of standards, and number of samples for each batch of samples run in your lab notebook.
2. Make sure to write down what you do at the time you do it. The sulfur coulometer is a bit finicky and writing things down can reduce headaches later.
3. Record any odd results or problems with the sulfur coulometer. If you are unsure of a result or something seems odd, we encourage you to ask questions. We want you to know that mistakes happen, even to those who have years of laboratory experience. The critical requirement is the mistakes be noted and discussed when they happen so corrections or adjustments can be made. It is generally best to start over.
4. All sample mass and sulfur results should be entered into the "Sulfur_Coulometry_Template" to obtain the %Total Sulfur (%TS) for each sample.
    a. It is best to enter the samples while running the instrument to ensure duplicates and standards fall within an acceptable range for each batch of samples.

Reagents Used

Reagents used are dispensed using the original holding container holding containers, squeeze bottles, or stainless steel spatulas. Reagents used as supplied by the manufacturer include anode solution (~30% Pyridine), anode solution (phosphoric acid), and vanadium pentoxide (neat solid). All reagents are pre-made by manufacturer, which requires no reagent preparation by lab technicians.

Equipment List

All necessary equipment is listed in the catalog with the exception of stainless steel spatulas and a squeeze bottles for methanol.

Procedure

**Instrument Set-Up**

1. Open the left furnace and check on the status of the reduced copper. It should appear shiny and bright. Blackened copper has been consumed. Either replace the copper with fresh reduced copper or reduce the existing copper with the procedure detailed below. Close the furnace.

2. Turn on the left and right furnaces. Resting temperature is 500□C. Heat the furnaces slowly. Increment in 100□C steps to set-point temperatures. The right furnace setpoint is 1050□, the left furnace set-point is 825□C.

3. Connect gas lines. Nitrogen (Ultra-High Purity) should be delivered at a pressure of 7-10 psi and then further adjusted to a flow of 100ml/min using the right hand regulator on the front of the combustion furnace. Oxygen (Ultra-High Purity) should be delivered at a pressure of 7-10 psi and further adjusted to a flow of 100 ml/min using the left hand regulator on the front of the combustion furnace. Hold the reset button in for three seconds while adjusting the oxygen flow.
    a. After setting the flow, the instrument will periodically admit oxygen to the combustion tube (you'll hear a clicking sound). Excess oxygen will consume the reduced copper prematurely!

4. Set up the coulometer.
    a. Mode selection thumb wheel position: 1 (units in display will be ugS)
    b. Time Set thumb wheel: 10 (minutes)
    c. Run/Latch switch: RUN
    d. Counts/Time: Counts (although it is OK to switch during run to see time elapsed)
    e. Cell filling:

        Anode (large side) – place a magnetic stir bar in the cell and fill with 50-100 ml of sulfur anode solution, insert the cell top (platinum anode electrode and dual platinum detector electrode), position the electrodes so the anode electrode is closest to the frit. The dual platinum detector electrodes should spaced about the width of a credit card apart from one another.

        Cathode (small side) – Fill with 12-20 ml sulfur cathode solution to the same level as the anode solution. Place the platinum cathode in the side arm with the platinum submerged in the solution.

    f. Place the assembled cell in the coulometer cell holder.

    Note: Mesh-type electrodes should be oriented parallel to the frit

5. Turning On Coulometer
    a. Turn off the coulometer cell current
    b. Turn on the main power switch
    c. Attach the anode and cathodes to the cell outlet terminals (they are color coded)
    d. Plug in the detector electrode
    e. Turn on the coulometer cell current
    f. Allow the cell current to titrate the solution to its endpoint (~6 □ amps)
    i. The anode solution should be a slightly yellow color when the titration reaches its endpoint

    Note: At this point, if the coulometer isn't titrating, delicately adjust the electrodes until they begin to titrate.

6. Blank Runs:
    a. Use an empty ceramic boat filled with a small amount vanadium pentoxide (as much as you would put on a regular sample).
    b. Put the ceramic boat with vanadium pentoxide in combustion tube and push into the combustion furnace using the medal sample rod. Close combustion tube as quickly as possible to reduce the loss of combusted sulfur.
    c. Press the reset button on the sulfur coulometer
    d. Wait 10 minutes and record the µg S in the "Sulfur_Coulometry_Template" . Blanks will range from 5 to 40 µg S

7. Sample Runs:
    a. Weigh sample out on a clean ceramic boat (50 to 150 mg depending on sulfur content)
    b. Cover sample completely with vanadium pentoxide
        i. To reduce the likelihood of spilling vanadium, pre-weigh all the samples you plan to run and place them in order (make sure to write down the order!) in secondary containment.
        ii. Place pre-weighed samples in the fume hood.
        iii. Put a lab coat, nitrile gloves, and lab goggles on before handling vanadium.
        iv. Cover each pre-weighed sample completely with vanadium pentoxide.
        v. Bring the samples back into the coulometry room in the secondary

containment

c. Put your first ceramic boat with sample and vanadium pentoxide in combustion tube and push into the combustion furnace using the medal sample rod. Close combustion tube as quickly as possible to reduce the loss of combusted sulfur.
d. Press the reset button on the sulfur coulometer
e. Wait 10 minutes (or until the µg S has changed less than 0.5% in 1 minute) and record the µg S in the "Sulfur_Coulometry_Template" as outlined in the Data

**Analysis section**

8. Standard runs: Precision and evaluation of the instrument set-up is determined by running sodium sulfate standard ($Na_2SO4$: 22.5% S) or sulfanilamide standard (18.6 % S). Accept results that are ± 5.0% of the expected S value. Weigh 3-7 mg of sodium sulfate and cover completely with vanadium pentoxide. Standards should be prepared in the same manner samples are prepared.

9. **Copper Reduction Method:**
   a. disconnect the Teflon tubing from the combustion tube outlet fitting
   b. furnaces should be at 500ºC
   c. turn off the oxygen flow
   d. fill the scrubber tube with 2-5 ml MeOH
   e. Insert a piece of Teflon tubing through the top piece of the scrubber extending to the bottom of the scrubber
   f. Disconnect the Teflon tubing from both the breech block inlet and the nitrogen gas exit connection.
   g. Use ¼" or 1/8" unions and 1/8" od. Teflon tubing to complete the following connections:
   h. Connect the nitrogen gas line to the top of the scrubber
   i. Connect the exit of the methanol scrubber to the combustion tube outlet fitting
   j. Connect the breech block inlet to a container filled with water
   k. Set the nitrogen flow to 100-150 ml/min on the instrument regulator (7-10 psi on the tank regulator) and allow the N2 to flow through the methanol until the copper is completely reduced.
   l. Add more methanol as need to the scrubber tube
   m. Water will accumulate in the right side of the combustion tube. Blot this away with a Kimwipe.

10. **Troubleshooting**
   a. Low results?
      i. leaks?
      ii. bad sample wt ?
      iii. not enough vanadium pentoxide
      iv. portion of evolved $SO_2$ missed ? (didn't close combustion tube promptly?)
      v. copper oxide consumed?
      vi. Reduced copper consumed?
   b. High results?
      i. bad sample wt ?
      ii. Takes too long to finish titration?
      iii. One of the electrodes flaky? Try very delicately touching the electrode wires.

Clean Up

1. Pour the used cathode and anode solutions into the appropriate waste container. Make sure the stir bar does not fall into the waste container (this is easily avoided by using a small necked funnel to transfer the anode solution to the waste container).
2. Rinse the cell and caps with water.
3. Pour methanol into the anode cell compartment. Use vacuum to pull the MeOH through the cell frit into the cathode compartment. Rinse with large volumes of DI water.
4. Keep S coulometry cell in dry storage area.
   a. Water left in glass frit will cause cathode solution to discolor during next use. It may be helpful to place S coulometry cell (empty) in a desiccator overnight before the next use.
5. Electrodes should be rinsed with DI water and blotted dry before storage.

Data Analysis

1. Enter your blank µg S reading and time into the "blank" column of the "Sulfur_Coulometry_Template". There will be no weight recorded for your blank.
   a. After you have blank entered into the spreadsheet, it will automatically correct each sample and standard.
2. Enter standard and sample mass, resultant µg S, and sample run time (the sulfur coulometer displays the sample run times) in the coulometer into the "Sulfur_Coulometry_Template".
   a. This spreadsheet will automatically calculate the %TS (equation below demonstrates the calculation the spreadsheet makes for you). Make sure that your standards and duplicates are within the acceptable range. If standards and duplicates are not within the acceptable range, samples must be run again.

Document History and References

Atkin, B. P., Somerfield, C., 1994. The determination of total sulphur in geological materials by coulometric titration. Chem. Geol., 111:131-134.

Wilkins, Bischoff, 2006. Coulometric determination of total sulfur and reduced inorganic sulfur fractions in environmental samples. Talanta 70(4):766-773.