The Johnson Company
ENVIRONMENTAL SCIENCE AND ENGINEERING SOLUTIONS

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August 10, 2007

USACE New England District: CENAE-EP-HE (ILIC)
ATTN: James Kelly
696 Virginia Road
Concord, MA 01742-2751

Subject: FINAL Sampling and Analysis Plan and Site-Specific Health and Safety Plan
Former Atlas S-11 Site, Ellenburg, New York
Contract W912WJ-05-D0006; Task Order 0004

Dear Mr. Kelly:

We are pleased to present the enclosed paper copy and CD of the Final Sampling and Analysis Plan (SAP) for the above-referenced project. This document has been prepared by the Johnson Company, Inc., and includes the following elements:

- A Site and Project Summary, (Sections 1.0 and 2.0)
- Work Management Plan, WMP (Sections 3.0 and 4.0)
- Field Sampling Plan, FSP (Sections 5.0 and 6.0)
- Quality Assurance Project Plan, QAPP (Sections 7.0 through 12.0)

The Final Site-specific Health and Safety Plan (HASP) is also enclosed for your files. The HASP is also included on a separate CD.

The Johnson Company performed an internal quality control check on the documents. This submission was subjected to review and coordination procedures to ensure: a) completeness for each discipline commensurate with the level of effort required for that submission; b) elimination of conflicts, errors, and omissions; and c) overall professional and technical accuracy. All comments received from the USACE have been addressed.

Sincerely yours,
THE JOHNSON COMPANY, INC.

By: _____
Donald Maynard, C.G., P.E., L.W.D
JCO Project Manager, Senior Geologist/Engineer
dmaynard@jcomail.com

Enclosure

CC (SAP only):
Helen Kim, New York District, Formerly Used Defense Sites Project Office
Russ Mulvey, New York DEC, Office of Environmental Quality, Region 5
Justin Deming, Public Health Specialist, Clinton County Health Department, New York State DOH
John Kanoza, P.E., C.P.G., Director/Engineer of Environmental Health, Clinton County Health Department
Ron Pentkowski, Severn Trent Laboratories, South Burlington, VT (CD only)
Bonnie Stadelman, Severn Trent Laboratories, Chicago, IL (CD only)

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Prepared for:
U.S. Army Corps of Engineers
New England District

FINAL
SAMPLING AND ANALYSIS PLAN ADDENDUM
FOR LONG-TERM MONITORING
FORMER ATLAS SITE S-11
ELLENBURG, NEW YORK

August 2007

Prepared by:

The Johnson Company
100 State Street, Suite 600
Montpelier, VT 05602

Task Order 0004
Contract W912WJ-05-D-0006
Document: K:\1-2128-5\Workplan\FinalWorkplan 080707.doc

The Johnson Company

COMMITMENT TO IMPLEMENT THE ABOVE SAMPLING AND ANALYSIS PLAN

Donald M. Maynard		8/8/07
Contractor's Project/Task Manager (print)	Signature	Date
James R. Bowes		8/8/07
Contractor's QC Manager (print)	Signature	Date
Other as Appropriate/Affiliation*(print)	Signature	Date
Other as Appropriate/Affiliation* (print)	Signature	Date
Other as Appropriate/Affiliation* (print)	Signature	Date

* Commitment signature is required for any ancillary sampling, analytical, or data assessment support provided by a contractor or subcontractor. For example, the Contractor's laboratory QC manager or director should sign the title page if analytical services are provided.

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1.0 INTRODUCTION

This Sampling and Analysis Plan addendum (SAP) has been prepared by The Johnson Company, Inc. (JCO) under contract with the U.S. Army Corps of Engineers (USACE) (Task Order 0004 of Contract W912WJ-05-D-0006). The SAP addendum has been prepared to address the "Statement of Work (SOW) for Groundwater Monitoring in Support of Site Closeout at Former Atlas Site S-11, Ellenburg, New York" issued by the United States Army Corps of Engineers (USACE) in February 2007, and revised March, 2007. The Atlas S-11 Site (the Site) location is shown on Figure 1-1. This document will serve as an addendum to the existing "Final Remedial Investigation Sampling and Analysis Plan" (Weston, July 2000) and "Draft Proposed Long-Term Monitoring Sampling and Analysis Plan" i.e., the Weston 2006 SAP (Weston, 2006a).

The February 2007 SOW consists of sampling two monitoring wells (MW-03 and MW-06) and four residential potable supply wells (locations 11, 35, 79, 80). However, access to MW-06 and to potable water supply wells 11 and 79 could not be obtained during the initial, July, 2006 long term groundwater monitoring event. The draft report of that event recommended sampling potable water supply wells 24, 68, and 118 in lieu of the inaccessible wells (Weston, 2006b). For that reason, this SAP includes those three wells in the monitoring program as shown in Figure 1-2.

A second change in this document from the Weston 2006 SAP, is the correction of the EPA Method 376.1 analysis to sulfide instead of sulfite. Sulfite was referenced incorrectly in the Weston document. Additionally, the holding time specified for this analysis was corrected from eight hours to seven days.

A third change in this document from the existing SAP prepared by Weston is a modification in the sampling schedule. The initially proposed schedule proposed the first monitoring round to be conducted in May, 2006 and for subsequent rounds to be collected on a

staggered schedule over the next three years to ensure that seasonal variation was taken into account during the long term monitoring program. However, the initial long term monitoring event did not occur until July 27, 2006 instead of May, and a second round was conducted on January 10, 2007. As a result, the seasonally staggered schedule of monitoring events has been altered as described below.

The six locations will be sampled six times over a period of approximately three years (Long-Term Monitoring [LTM]) utilizing the July 2006 and January 2007 events as the first two events. Results of each round will be summarized in groundwater summary reports after they are received. The rounds of sampling will be staggered so as to represent each season of the calendar year (e.g., July of 2006, January, May/June and October of 2007, and February and August of 2008). After the sixth round of sampling, the groundwater data will be evaluated to determine if additional monitoring is necessary.

The planned field work will be performed in accordance with the USACE SOW (USACE 2007) except for variations in the sample locations and dates as described above. Specific procedures for each element of the field program are provided in the Standard Operating Procedures (SOPs) and Site Specific Methods (SSMs), and clarified in the body of this document. At the direction of the US ACE, a large portion of this document was copied directly from the Weston 2006 SAP prepared under contract to the US ACE, Contract No. W912DR-05-D-0022.

The remainder of this Section 1.0 provides a brief summary of Site conditions, previous investigations and remedial actions. Section 2.0 provides the project objectives, and Section 3.0 the roles and responsibilities of the project team. The other sections of this SAP provide the field and analytical laboratory methods and procedures that will be implemented for this phase of field data acquisition.

1.1 SITE DESCRIPTION AND BACKGROUND

Atlas S-11, shown in Figure 1-1, is located in the hamlet of Ellenburg Depot, in the town of Ellenburg, New York and was originally acquired in 1960 by the Department of Defense (DOD) for the purpose of constructing a missile launching facility. By September 1965, all Atlas intercontinental ballistic missile (ICBM) sites in what was known as the Plattsburgh complex (including Atlas S-11) were deactivated. Environmental studies conducted to date have indicated the presence of trichloroethene (TCE) in groundwater on and off site. Weston Solutions, Inc. (Weston®), under contract by the USACE New England District (NAE), carried out a remedial investigation (RI) involving environmental evaluations of soil, sediment, surface water, and groundwater associated with Atlas S-11. The focus of this investigation was to evaluate the extent of TCE contamination and its potential impact to downgradient areas.

The RI activities were conducted by Weston between December 1998 and September 2003. The investigation consisted of the following:

- Four quarterly rounds of residential water supply well sampling in the hamlet of Ellenburg Depot. The purpose was to characterize the nature and extent of contamination in areas within the hamlet and provide information to support planning of additional field investigations.
- Geophysical surveys conducted at Atlas S-11 and within Ellenburg Depot to identify potential source areas/materials and provide other information regarding subsurface conditions at the site.
- A soil gas survey conducted at the site to identify potential sources and further aid in the placement of test pits and groundwater monitoring wells.
- A test pit investigation of the anomalies identified during the geophysical surveys at Atlas S-11 and potential sources of TCE detected during the soil gas investigation.
- Installation of a groundwater monitoring well array across Atlas S-11 and Ellenburg Depot followed by two rounds of groundwater sampling to better understand the direction of groundwater flow, determine migratory pathways, and establish the distribution of contamination in the aquifer. Four additional rounds of sampling were collected from the array to determine the seasonal variation and supplement information regarding the low concentrations of TCE detected during the initial two rounds.

2.0 PROJECT OBJECTIVES

The overall objectives of this phase of the project are to complete field data requirements necessary to:

1. Determine if contamination is present in groundwater above Maximum Contaminant Levels (MCLs);

2. Determine if conditions suitable for in-situ natural attenuation by biodegradation are present in groundwater.

The new tasks included in this addendum consist of the re-establishment of the well sampling program (semi-annually for three years) and preparation of groundwater monitoring reports. These additional tasks are necessary to ensure no unacceptable public health risks exist due to TCE contamination found in the fractured bedrock at Atlas S-11. The sampling program will consist of six rounds of sampling from the one monitoring well and five residential supply wells identified in Figure 1-2.

3.0 PROJECT ORGANIZATION AND RESPONSIBILITIES

The project is being performed for the USACE New England District. The USACE will provide execution and technical oversight as well as administrative support and review. USACE team members and contact information are provided in Table 3-1.

Table 3-1
USACE Team Members

Title	Name	Phone Number	Email
Project Manager	James Kelly	978-318-8227 Fax 978-318-8614	James.A.Kelly@nae02.usace.army.mil
Project Chemist	David Lubianez	978-318-8311	David.J.Lubianez @nae02.usace.army.mil
Field Geologist	Paul Young	978-318-8597	Paul.J.Young@nae02.usace.army.mil
Health & Safety Officer	Sheila Harvey	978-318-8504	Sheila.Harvey@nae02.usace.army.mil
Risk Assessor	Cliff Opdyke, Ph.D	502-315-6314	Cliff.Opdyke@lrl02.usace.army.mil
NY Project Manager	Helen Kim	732-435-0079	Helen.Kim@usace.army.mil

The project is being performed under the authority of the New York State Department of Environmental Conservation (NYS DEC). The NYS DEC project manager is Russell Mulvey (518-897-1241). The New York State Department of Health (NYS DOH) and the Clinton County Health Department also have an interest in the project. The NYS DOH contact is Justin Deming, Public Health Specialist. The Clinton County Health Department contact is John Kanoza, P.E., C.P.G., Director/Engineer of Environmental Health.

The following paragraphs describe the project team, consisting of selected representatives from the Johnson Company, Inc.

3.1 THE JOHNSON COMPANY

Key personnel for field operations and their specific responsibilities are discussed below. Table 3-2 includes names and contact information.

Table 3-2 Project Organization					
Title	**SSO**	**Name**	**Phone Number**	**Office/Cell Number**	**Email**
Project Manager		Donald Maynard	802-229-4600	802-272-8868	dmaynard@jcomail.com
Corporate QA Officer		James Bowes	802-229-4600	Not Available	jbowes@jcomail.com
Health & Safety Officer		Joel Behrsing	802-229-4600	Not Available	j-behrsing@jcomail.com
Field Task Manager	X	Thomas Osborne	802-229-4600	802-249-2630	TRO@jcomail.com
Senior Technician	X	Warren Davey	802-229-4600	802-223-4502	WPD@jcomail.com

Project Manager (PM)

The PM organizes the assigned project staff and initiates project planning and implementation activities at the Task Order level. The PM controls the budget and schedule ensuring that contract requirements are met. Mr. Maynard is responsible for managing all field activities related to the requirements of the project, including subcontractors. The PM is responsible for ensuring that all project activities conform to USACE requirements and specifications and that field data acquisition conforms to data needs. PM duties also include the assignment of responsibilities for the preparation of the various reports and the review of each form/report for accuracy and content. The PM also has primary responsibility of tracking any proposed changes in the scope of work (SOW) for the overall project and will report any proposed changes to USACE.

Field Task Manager (FTM)

The FTM is responsible for desktop planning, equipment procurement, scheduling, subcontracting, and mobilization for this field program including planning and coordination of sampling activities. The FTM has overall responsibility for completion of all field activities in accordance with this SAP. With the oversight of the QAO, the FTM is also responsible for ensuring that field personnel properly implement SAP procedures as they apply to field sampling, monitoring, and analysis processes. Specific responsibilities of the Field Task Manager include:

- Coordinating activities in the field;
- Assigning specific duties to field team members;
- Mobilizing and demobilizing of the field team and subcontractors;
- Directing the activities of subcontractors in the field;
- Resolving any logistical problems that could potentially hinder field activities, such as equipment malfunctions or availability, or weather dependent working conditions; and
- Coordinating with the QAO (see below) in implementing field quality control (QC) including issuance and tracking of measurement and test equipment; proper equipment calibration and sampling procedures, the proper labeling, handling, preservation, storage, shipping, and chain-of-custody procedures used at the time of sampling; and control and collection of all field documentation.

Quality Assurance Officer (QAO)

The QAO is responsible for the project quality assurance/quality control (QA/QC) in accordance with this SAP and appropriate management guidance. The QAO will ensure that the project field activity readiness review is conducted; approve variances during field activities before work continues; approve, evaluate, and document the disposition of non-conformance reports (NCRs). He will also oversee and approve any required project training, design audit/surveillance plans, and subsequently supervise these activities. The QAO will be responsible for coordinating the analytical services, the acquisition and delivery of sample bottles to the site, and validation of the analytical data.

Health & Safety Officer (HSO)

The HSO will be responsible for ensuring that health and safety procedures designed to protect personnel are maintained throughout the field activities conducted for this project. This will be accomplished by strict adherence to the project specific Health and Safety Plan (HASP). The HSO will also be responsible for the coordination and communication of health and safety issues for field personnel.

Site Safety Officer (SSO)

All field personnel are responsible for implementing the safety requirements specified in the HASP for field activities. However, one person will be designated to serve as the SSO on each field day. The SSO will be appointed by the PM. The SSO will be on-site during all JCO activities covered by this SAP. The SSO is responsible for enforcing the requirements of the HASP once work begins. The SSO has the authority to immediately correct all situations where noncompliance with the HASP is noted and to immediately stop work in cases where an immediate danger is perceived. Additional responsibilities are outlined in the HASP.

Field Staff

The field staff reports directly to the FTM. The responsibilities of the field team include:

- Collecting samples, conducting field measurements, and decontaminating sampling equipment according to documented procedures stated in this SAP;
- Ensuring that field instruments are properly operated, calibrated, and maintained, and that adequate documentation is kept for all instruments;
- Collecting the required QC samples and thoroughly documenting QC sample collection;
- Ensuring that field documentation and data are complete and accurate;
- Ensuring that all health and safety protocols are followed for JCO field activities, in accordance with the project specific HASP; and
- Communicating any nonconformance or potential data quality issues to the FTM and QAO.

3.2 OTHER (NON-JCO) CONTRACTORS

JCO has retained subcontractors in order to complete the requirements of the SOW. A description of these subcontractors and their responsibilities is presented below. JCO will also provide support as directed by USACE in coordinating with and participating in any work performed by the USACE and its contractors for field activities coincident with and independent of the effort discussed in this SAP. The roles of the JCO subcontractors are as follows:

Laboratory Contractor

Severn Trent Laboratories (STL), Burlington, South Burlington, Vermont and STL Chicago will be the contract laboratories for analysis associated with Atlas S-11. Both STL laboratories have been validated by the USACE, Hazardous, Toxic and/or Radioactive Waste-Center of Expertise (HTRW-CX), Omaha, Nebraska, and are approved to perform the analyses required under this SAP, where applicable. The prime subcontractor laboratory contact for this project is Mr. Ron Pentkowski, (802) 660-1990 [RPentkowski@stl-inc.com] in Burlington, Vermont. STL Burlington will perform the majority of the analysis, with STL Chicago performing the sulfate, sulfide, nitrate and nitrite analyses. The laboratory contact information is:

STL Burlington, 30 Community Drive, Suite 11
South Burlington, VT 05403
Telephone: 802-660-1990 Fax: 802-660-1919

The Chicago STL point of contact is:

Ms. Bonnie Stadelman - Project Manager
bstadelman@stl-inc.com
STL Chicago, 2417 Bond Street
University Park, IL 60466
Phone:708-534-5200

4.0 TASK SCOPES AND OBJECTIVES

The field activities conducted and chemical data collected during this effort will be used for the following purposes:

- Ensure that no unacceptable public health risks are present due to TCE contamination in the fractured bedrock at Atlas S-11.
- Evaluate natural attenuation processes that may be occurring in groundwater to determine if monitored natural attenuation (MNA) is a viable long-term groundwater remedy.
- Form a basis for evaluating remedial alternatives.

Groundwater sampling will be conducted to further understand the existence of contamination and to generate data of known and defensible quality. A summary of the proposed sampling locations and objectives is provided in Table 4-1. The sampling and analytical program is designed to achieve the objectives discussed above and to ensure consistency with applicable regulations and guidance documents.

Table 4-1
Laboratory analysis methods and expected numbers of samples per monitoring event

Parameters	**Preparation / Analysis Method**	**#Field Samples**	**QA/QC Samples**			**Totals**
			Duplicate /Replicate	**Field Blank/ Trip Blank**	**MS/ MSD**	
VOCs	EPA Method 524.2	SIX TOTAL *PW-68 PW-80 PW-35 MW-3 PW-118 PW-24*	1	1/1	1/1	11
ammonia	EPA Method 350.2		1	1	1/1	10
methane/ethane/ethene	Method RSK-175					
nitrate/nitrite	EPA Method 353.2					
total phosphorous	EPA Method 365.2					
sulfate	EPA Method 375.4					
sulfide	EPA Method 376.1					

4.1 CHEMICAL DATA QUALITY OBJECTIVES

The desired data quality will be attained through compliance with the quality assurance/quality controls protocols described in this SAP. A description of the data to be collected and required minimal data quality is provided below.

Field measurements of groundwater parameters will be performed to assess if in-situ conditions are suitable for the natural attenuation of chlorinated solvents. Results of these tests, in conjunction with laboratory analysis of additional monitored natural attenuation (MNA) parameters will be compared to the EPA *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (US EPA, 1998) in order to determine the likelihood of TCE undergoing significant degradation in the subsurface.

Groundwater parameters will be monitored in the field during low-flow purging using a calibrated water quality meter until stabilization is achieved. Field test kits will be used to measure the MNA parameters alkalinity, carbon dioxide and ferrous iron following stabilization. The following detection limits/precision are required for these analyses based upon the results of previous monitoring events and the EPA Technical Protocol (EPA, 1998) cited above (Tables 2.2 and 2.3):

- dissolved oxygen (DO) 0.2 milligrams per Liter (mg/L), +- 0.2 mg/L;
- oxidation-reduction potential (ORP) +-50 millivolts (mV);
- pH +- 0.1 standard units
- temperature 0 degrees C, +- 1 degree C
- Conductivity 50 micro siemens per square centimeter (uS/cm^2), +- 50 uS/cm^2
- alkalinity 10 mg/L, +- 20 mg/L
- carbon dioxide 10 mg/L, +- 10 mg/L
- ferrous iron 0.5 mg/L, +- 20%

A sample will be collected from each location for laboratory analysis for the MNA parameters listed below. The following method detection limits/precision are required for these analyses based upon the results of previous monitoring events and the EPA Technical Protocol (EPA, 1998) Table 2.2:

- ammonia by EPA Methods 350.2 — 25 micrograms per Liter (ug/L); +- 20%
- methane/ethane/ethene by Method RSK-175 — 1 ug/L +-20%;
- nitrate/nitrite by EPA Method 353.2 — 100 ug/L, +- 100 ug/L;
- total phosphorous by EPA Method 365.2 — 100 ug/L; +- 20%
- sulfate by EPA Method 375.4 — 5 mg/L, +- 20%
- sulfide by EPA Method 376.1 — 500 ug/L, +- 20%

A sample will be collected from each location for laboratory analysis for Target Compound List (TCL) Volatile Organic Compounds (VOCs) by United States Environmental Protection Agency (EPA) Method 524.2. Detections of TCE and associated breakdown products considered to be DOD-related contaminants of concern (COCs) will be compared to the both EPA Code of Federal Regulations (CFR) Title 40, Part 141.61, National Primary Drinking Water and NYSDEC Rule and Regulations (NYCRR) Part 703, Chapter X, Surface Water and Groundwater Quality Maximum Contamination Levels (MCLs).

All laboratory method detection limits (MDLs) are required to be below the respective standards of each compound. Table 4-2 lists both EPA and NYSDEC criteria as well as the required MDLs. Guidance values set by the NYSDEC Technical Operations Guidance Series, Part 1.1.1 (TOGS) are non-enforceable and are listed for reference. Note that concentrations present below the detection limits (PQLs) will be reported by the laboratory as estimated values.

Table 4-2
Summary of EPA and NYSDEC Criteria for VOC in Groundwater
Long-Term Monitoring, Former Atlas Site S-11, Ellenburg, New York

Target Compound List	CAS Number	EPA MCL Criteria (ug/L)	NYSDEC Rule and Regulation Criteria (ug/L)	NYS TOGS Values[1] (ug/L)	Practical Quantitation Limit (ug/L)	Method Detection Limit (ug/L)
Acetone	67-64-1			50	5.0	2.22
Benzene	71-43-2	5	1		1.0	0.21
Bromodichloromethane	75-27-4			50	1.0	0.13
Bromoform	75-25-2			50	4.0	0.21
Bromomethane	74-83-9		5		5.0	0.42
2-Butanone	78-93-3			50	5.0	1.03
Carbon Disulfide	75-15-0			60	5.0	0.64
Carbon Tetrachloride	56-23-5	5	5		5.0	0.16
Chlorobenzene	108-90-7	100	5		2.0	0.16
Chloroethane	75-00-3		5		5.0	0.32
Chloroform	67-66-3		7		5.0	0.20
Chloromethane	74-87-3		5		5.0	0.36
Dibromochloromethane	124-48-1			50	5.0	0.12
1,1-Dichloroethane	75-34-3		5		5.0	0.16
1,2-Dichloroethane	107-06-2	5	0.6		2.0	0.29
1,1-Dichloroethene	75-35-4	7	5		2.0	0.21
cis-1,2-Dichloroethene	156-59-2	70	5		5.0	0.22
trans-1,2-Dichloroethene	156-60-5	100	5		5.0	0.16
1,2-Dichloropropane	78-87-5	5	1		1.0	0.18
cis-1,3-Dichloropropene	10061-01-5		0.4 (cis & trans)		5.0	0.13
trans-1,3-Dichloropropene	10061-02-6		0.4 (cis & trans)		5.0	0.17
Ethylbenzene	100-41-4	700	5		4.0	0.12
2-Hexanone	591-78-6			50	5.0	1.21
Methylene chloride	75-09-2	5	5		3.0	0.26
4-Methyl-2-pentanone	108-10-1				5.0	0.94
Styrene	100-42-5	100	5		5.0	0.18
1,1,2,2-Tetrachloroethane	79-34-5		5		1.0	0.20
Tetrachloroethene	127-18-4	5	5		1.0	0.22
Toluene	108-88-3	1,000	5		5.0	0.20
1,1,1-Trichloroethane	71-55-6	200	5		5.0	0.27
1,1,2-Trichloroethane	79-00-5	5	1		3.0	0.29
Trichloroethene	79-01-6	5	5		1.0	0.14
Vinyl chloride	75-01-4	2	2		5.0	0.29
o-Xylene	95-47-6	10,000 total	5 (each, o, m and p)		5.0	0.26
m,p-Xylene		10,000 total			5.0	0.42

[1] Non-enforceable guidance value published in NYSDEC Division of Water Technical Operational Guidance Series 1.1.1 "Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations"
Blank cells indicate criteria for that compound not available for that regulation or rule.

4.2 SCHEDULE

Field activities are anticipated to commence in May/June 2007. The following outline is an estimate of time requirements for implementation of this work plan.

- Notifications: Notifications to the USACE Engineering Manager and New York State Department of Environmental Conservation (NYSDEC) Point of Contact (POC; Russell Mulvey, 518-897-1241) will be made at least one week in advance of all on-site activities. The USACE Engineering Manager and the NYSDEC POC will also be provided at least a 24-hour notice if any activity is cancelled.

- Mobilization and Site Preparation: Prior to site activities, mobilization activities including planning and scheduling, subcontracting, subcontractor coordination, equipment procurement, and other preparatory tasks will be performed.

- Groundwater Sampling: The first round of monitoring well sampling following the July 2006 and January 2007 events is scheduled to be completed in May/June 2007. Subsequent rounds will be conducted in October of 2007, and February and August of 2008.

- Groundwater Analytical Results: Analytical results from groundwater sampling activities will be received within three weeks of completion of field activities.

- Draft Groundwater Monitoring Report: The draft groundwater monitoring report will be submitted to USACE within 45 days of sample collection following completion of each sampling event round. The report will describe the field activities conducted, present findings in narrative, tabular and graphical form, and provide an interpretation of the data with conclusions and recommendations including: 1) a discussion of the significance of the analytical results; 2) a data evaluation ; 3) a table summarizing the results of each sample (this table shall include each round of sample results and be successively updated with each sample round so that a comparison of results from each sample round can be made with all previous rounds); 4) a copy of the primary laboratory report; 5) a map showing sample locations and results, including figures or plots of TCE versus breakdown /daughter products for each of the 6 groundwater sample locations; and 6) A discussion of natural attenuation and indicator results.

- Final Draft Groundwater Monitoring Report: The final draft groundwater monitoring report will be submitted to USACE, NYSDEC and NYS DOH three weeks after receipt of USACE comments on the draft report.

- Final Groundwater Monitoring Report: The final groundwater monitoring report will be submitted to USACE, NYSDEC and NYS DOH three weeks after receipt of all comments on the final draft report.

5.0 FIELD ACTIVITIES

This section specifies procedures for the following field activities:

- Groundwater Sampling
- Laboratory Analysis and Field Testing
- Decontamination

Proposed sampling locations are depicted in Figure 1-2. Site Specific Methods (SSMs) and Standard Operating Procedures (SOPs) are provided in Appendix 1. Contact information for the property owners of the six sampling locations is provided below:

PW-24

Poulin Grain Hardware
Jim Dominic (owner/operator)
33 Canaan Road
Ellenburg Depot, NY 12935
(518) 594-3922
Sample at spring at gazebo (flowing well)

PW-35

Mr. and Mrs. LaFave
5076 Route 11
Ellenburg Depot, NY 12935
(518) 594-7042
Sample at bypass spigot in basement

PW-68

Varin's Market
Derrick Varin (Owner/Operator)
5047 Route 11
Ellenburg Depot, NY 12935
(518) 594-3972
Sample at bypass spigot in basement right next to the pump

PW-80

Baker Commodities – Division of Ellenburg Recycling
(former Northland Hides)
Mark Rowe and Jane Rowe
Ellenburg Depot, NY 12935
24 Station Hill Road
518-594-3900
Sample at kitchen tap in main office building.

PW-118

PW-118 is owned by Cynthia Rowe, however, the house is rented out.
29 Station Hill Road
Ellenburg Depot, NY 12935
Sample at bypass spigot in basement

MW-3

Cynthia Rowe (Property Owner, also owns property for PW-118)
18 Grace Avenue
Plattsburg, NY 12901
(518) 561-8175
Low-Flow Sampling after Parameter Stabilization

5.1 SAMPLING FOR LABORATORY ANALYSIS AND FIELD TESTING

All samples will be collected, stored and transported in accordance with SOP-JCO-007 Chain of Custody (COC) procedures. Records of sample collection will be maintained in a bound field book in accordance with SOP-JCO-034, Use of Field Log Books.

5.1.1. Sample designation

Samples collected under this work plan will be uniquely identified according to the round number, type of sample, and location number using the following scheme:

GW#-A-CCCCC-XXX

- Sequential number indicating the round of groundwater sampling beginning at 9 in May/June, 2007 to account for the previous eight rounds already collected.

A - 0 for field sample, 1 for duplicate, matrix spike, or matrix spike duplicate sample, and 2 for a field rinsate blank sample.

CCCCC - Location of sample (e.g. MW-03 or PW-11).

XXX - FB for field rinsate blanks, MS for matrix spike samples, MSD for matrix spike duplicates, DP for duplicate samples (VOCs) and RP for replicate samples (metals only)

For example, a monitoring well sample collected from MW-03 during the proposed May/June, 2007 sampling event would have a designation GW9-0-MW-03. The sample collected during the same round for a duplicate from the potable supply well number 68 (Figure 1-2) would be labeled GW9-2-PW-68-DP.

Trip blank samples will be denoted with "TB" after the *GW#* designation followed by the date that the first sample was added to the associated cooler. For example, the trip blank for samples collected June 1, 2007 would be identified as GW9-TB-060107.

5.1.2 Equipment Use, Calibration and Maintenance

All monitoring equipment used on-site will be maintained, calibrated and operated in accordance with the manufacturer's specifications, the National Field Manual for the Collection of Water-quality Data (USGS various dates), EPA Region 1 Guidelines, USGS Techniques of Water-Resources Investigations, Book 9, Chapters A1-A9, and the JCO SOPs and SSMs included in Appendix 1. All field water quality measurements and related instrument calibrations will be performed in accordance with:

- http://pubs.water.usgs.gov/twri9A. [Chapter updates and revisions are ongoing and are summarized at http://water.usgs.gov/owq/FieldManual/mastererrata.html]
- Manufacturer recommendations
- EPA Region I Guidelines

The Standard Hydrogen Electrode conversion will be done for final ORP measurements in accordance with the manufacturer's documentation, with constants and equations documented in the report.

5.1.3 Groundwater sampling

Groundwater samples will be collected from five water supplies and from the monitoring well MW-3. The field sheets from the July, 2006 sampling event of these wells are included in Appendix 2. The existing pumps and plumbing will be used to sample the water supply wells. A 2-inch Grundfos Redi-flo 2 pump will be used with dedicated tubing to sample MW-3. MW-3 is reported to be 136.7 feet deep below the top-of-casing. The depth of the sample pump intake in MW-3 will be approximately 136 feet below the top of PVC casing. The order of sampling (based upon sampling the least likely contaminated to the most likely contaminated well) is preferred to be:

PW-68 Varin market
PW-80 Baker Commodities
PW-35 LaFave

MW-3 Rowe/LaFountain
PW-118 Rowe/LaFountain
PW-24 Poulin Grain

Because the historical detections of TCE in all of these wells have been below 3 ug/L, it is permitted to change the preferred order of sampling in the field if conditions (such as access) warrant.

The hydraulic head, i.e., depth to static water level, will be measured in MW-3 immediately prior to purging and sampling. The measurement of hydraulic head will be performed with an electronic water marker in accordance with SOP-JCO-009 (For Water Level Measurements). No attempt will be made to measure the hydraulic head in the water supplies, due to the likelihood of snaring the water marker on the well pump pipe, electrical wires and/or stabilizers.

Monitoring well MW-3 will be purged and sampled in accordance with SSM-JCO-053 Slow Purge Groundwater Sampling using a downhole pump and dedicated polyethylene tubing. Prior to use, the pump will be decontaminated in accordance with the July 30, 1996, Revision 2, US EPA Region 1 Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells and SSM-JCO-027 for Decontamination of Equipment (included in Appendix 1), including pumping the decontamination fluids through the pump, with Alconox^{TM} and water, followed by a triple rinse with distilled water. Samples will be collected with the pump after purging is complete and groundwater field parameters have reached equilibrium.

For all wells, field measured indicator parameters (pH, temperature, specific conductance, oxidation-reduction potential, and dissolved oxygen) will be monitored during purging using a YSI Multi-Parameter Probe. Turbidity will be separately monitored using a HF Scientific Model DRT-15CE or Lamotte 2020 turbidimeter, or its equivalent. The parameters will be monitored for stabilization in accordance with the EPA Region 1 Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells, July 30, 1996,

Revision 2, prior to collection of the sample. All field measured data will be recorded on form JCO-HYDRO-10 (included with EPA Low Purge Method in SSM-JCO-053).

Stabilization is considered to be achieved when three consecutive readings, measured at 3 to 5 minute intervals, are within the following limits:

- Turbidity = +/- 10% for values between 1 and 100 NTU or less than 1 NTU
- DO = +/-0.3 mg/L
- Specific conductance =+/-3%
- Temperature = +/- 0.2 degrees C
- pH = +/- 0.1 units
- ORP = +/- 10 millivolts
- Drawdown = minimum drawdown with linear rate of head decline

The low-flow guidance suggests a maximum drawdown of 0.3 feet. However, in fractured bedrock, it is not uncommon to observe greater drawdown under low flow pumping conditions. JCO will carefully monitor hydraulic head in MW-3 and seek a purge rate that will minimize drawdown. If head continues to decline the JCO will calculate the rate of decline. Once this rate has stabilized for 3 consecutive readings, and a minimum of three well volumes of water has been removed, JCO will consider this criterion to be satisfied. This criteria does not apply to the water supply wells.

All field water quality parameters will be collected in accordance with USGS parameter-specific protocols and SSM-JCO-053. Final water quality testing results for groundwater will be reported as field results and Standard Hydrogen Electrode adjusted values (equations and constants used will also be reported).

Field test kits will be used to measure the MNA parameters alkalinity, carbon dioxide and ferrous iron following stabilization. Details of the methods to be used are provided in SSM-JCO-053. Total alkalinity will be measured using the CHEMetrics K-9810 titration method (MDL = 10 mg/L) which is based upon ASTM D 1067-92, Acidity or Alkalinity of Water; APHA Standard Methods, 19th ed., p. 2-26, method 2320B (1995); and EPA Methods for Chemical Analysis of Water and Wastes, Method 310.1 (1983). Dissolved carbon dioxide will

be measured using the CHEMetrics K-1910 titration method (MDL = 10 mg/L) which is based upon APHA Standard Methods, 19th ed., p. 4-17, Method 4500-CO2 C (1995); and ASTM D 513-82, Total and Dissolved Carbon Dioxide in Water, Test Method E. Ferrous iron will be measured using a HACH DR890 colorimeter and the Hach Iron Ferrous Reagent, 1,10 Phenanthroline, AccuVac® Ampules (detection limit of 0.3 mg/L).

Water supply wells will be sampled from the existing plumbing as close to the well head as possible using available bypass spigots or faucets. Whenever possible, the same locations and flow rates described above and in the field sheets included in Appendix 2 will be used to collect the samples. Every reasonable effort will be made to bypass treatment systems or aerators inline with the supply well without jeopardizing the safety of personnel or integrity of the supply systems. Wells will be purged for a minimum of 15 minutes. Water will be continually monitored for the same parameters and using the same methods as those used in monitoring well sampling. After purging is complete, samples will be collected for the parameters listed in Table 4-1 from a slow stream of water in order to minimize turbulence.

In July, 2006, the potable wells were purged, via the holding tank/filtration bypass spigots except for PW-80 and PW-24. Location PW-80 was the only well sampled using a sink faucet being that it did not have a tank/filtration system or bypass. In the case of PW-24, the well is under positive pressure naturally (flowing artesian) so a sample was collected at the spring outfall pipe along Canaan Road (Figure 1-2).

5.2 LABORATORY ANALYTICAL TESTING

All laboratory testing will be performed by Severn Trent Laboratories (STL). All of the analyses will be performed at the Burlington, Vermont lab except wet chemistry methods including Sulfide by Method 376.1, Sulfate by Method 375.4 and Nitrate/Nitrite-N by Method 353.2. These methods will be tested at STL Chicago, as were the previous long term monitoring samples.

Both STL Burlington and STL Chicago are considered in compliance with the DoD Quality Systems Manual for Environmental Laboratories and hold an unexpired USACE Environmental Laboratory validation and are therefore grandfathered as meeting this policy, until such time as their validation term expires. Tables 4-1 and 4-2 provide details of the required chemical testing.

6.0 FIELD OPERATIONS, DATA DOCUMENTATION AND MANAGEMENT

This section describes the required elements of daily record keeping and project tracking.

6.1 DAILY REPORTS AND MEETINGS

JCO will conduct a daily project briefing and health and safety meeting with on-site personnel. At the conclusion of each day, a short meeting will be held to coordinate activities and schedules for the next day. Daily reports of work performed will be faxed or E-mailed to the US ACE Engineering Manager within 24 hours during the field activities outlined in this SAP. The reports will include a summary of each day's activities including the number of analytical samples collected. Completed chain-of-custody forms will be attached to the report as appropriate. Departures from the approved SAP will be documented in the reports. Significant problems and corrective actions taken will be reported to the US ACE within 24 hours of occurrence.

6.2 FIELD RECORDS

Field logbooks will provide the means of recording the data collection activities performed during the investigation. As such, entries will be described in as much detail as possible so that persons going to the site could reconstruct a particular situation without reliance on memory. Field logbooks will be bound field survey books or notebooks. Logbooks will be assigned to field personnel. Each logbook will be identified by the Site name and a unique sequential number (e.g. the first log book will be *Atlas S-11 #1*). Further discussion of field log book requirements is presented in Section 9.2. Field logbooks will be supplemented by standardized field measurement and sample collection forms where appropriate. Sample collection forms are provided in SOPs and SSMs included in Appendix 1.

All entries will be made in permanent ink, signed, and dated and no erasures or obliterations will be made. If an incorrect entry is made, the information will be crossed out with a single strike mark which is initialed and dated by the sampler. Whenever a sample is collected, or a measurement is made, a detailed description of the sampling location will be recorded or referenced. The number and direction of photographs taken of the sampling location, if any, will

be noted. The equipment used to make measurements will be identified, along with the date of calibration (unless otherwise documented on applicable forms).

6.3 HEALTH AND SAFETY

A Site Specific Health and Safety Plan (HASP) has been prepared and will be made available to, and reviewed with, all on-site personnel. It is anticipated that all work will be conducted under Level D. Site work will not commence until US ACE acceptance of the HASP has been received.

6.3.1 Accident Prevention Plan

An Accident Prevention Plan (APP) specific to the activities being performed has been prepared and is included in the Site Specific Health and Safety Plan. It includes an Activity Hazard Assessment (AHA) as described below. All work shall be conducted in accordance with the APP, USACE Safety and Health Requirements Manual (EM 385-1-1, most recent edition), and all applicable federal, state, and local safety and health requirements.

The APP shall detail how safety and health will be managed during the project. The APP shall address the requirements of applicable Federal, State and local safety and health laws, rules, and regulations. The Site Health and Safety Officer shall conduct a safety meeting at the project site on each day of work. All safety meetings shall be documented.

6.3.2 Activity Hazard Assessment

An AHA has been prepared for each major phase of work and is included in the Site Specific Health and Safety Plan (HASP). A major phase of work is defined as an operation involving a type of work presenting hazards not experienced in previous operations or where a new subcontractor or work crew is to perform the work. The analysis defines all activities to be performed, identifies the sequence of work, the specific hazards anticipated, and the control measures to be implemented to eliminate or reduce each hazard to an acceptable level.

A preparatory meeting shall be conducted by the Site Health and Safety Officer to discuss the AHA contents with all engaged in the activity. The preparatory meeting will include any on-site subcontractors and Government on-site representatives. The AHA shall be continuously reviewed and revised to address changing site conditions or operations as appropriate.

6.3.3 Accident Reporting

All accidents and near misses (near hits) shall be investigated by the Site Health and Safety Officer. All work-related recordable injuries, illnesses and property damage accidents (excluding on-the-road vehicle accidents), in which the property damage exceeds $2,000.00, shall be verbally reported to the US ACE within 24 hours of the incident. Serious accidents as described in EM 385-1-1 Section 01.D.02 shall be immediately reported to the US ACE.

7.0 ANALYTICAL METHODOLOGY, DATA QUALITY LEVELS, AND REPORTING

Groundwater samples are proposed to be collected from six selected wells and analyzed for the parameters listed in Table 4-1. Trip blanks, equipment blanks, injection water, field duplicates, replicates and matrix spike/matrix spike duplicates (MS/MSDs) associated with the groundwater samples will also be collected and submitted for analysis at the frequency discussed below.

Non-detect results for all parameters will be reported at the laboratory's practical quantitation limit (PQL). Estimated values (J flagged) will be reported for concentrations detected between the PQL and the method detection limit (MDL).

Laboratory data reduction procedures will be performed according to the following protocol. Information related to analysis will be documented in controlled laboratory logbooks, instrument printouts, or other approved forms. All entries that are not generated by an automated data system will be made neatly and legibly in permanent, waterproof ink. Information will not be erased or obliterated. Corrections will be made by drawing a single line through the error and entering the correct information adjacent to the cross-out. All changes will be initialed, dated, and, if appropriate, accompanied by a brief explanation. Unused pages or portions of pages will be crossed out to prevent future data entry. Analytical laboratory records will be reviewed by the supervisory personnel on a regular basis, and by the Laboratory QA Coordinator periodically, to verify adherence to documentation requirements.

Analytical data deliverables will be provided to JCO within standard turnaround time (not to exceed three weeks) from date of sample receipt at the laboratory. The laboratory will provide at least one copy of hard copy report and one copy of an electronic data deliverable (EDD). The hard copy data package will be equivalent to a Contract Laboratory Program (CLP) deliverable, i.e., consisting of all the information presented in a CLP package, including CLP-like summary forms. This information is summarized below:

- Cover page including title of report; name and location of laboratory; contact information; name and location of any subcontractor laboratories; contract number; unique ID for the

report; client name and address; project name and site location; statement of authenticity and signature/title of person releasing report; and total number of report pages
- Table of contents
- Case narrative (see description below)
- Cross reference of field sample IDs and laboratory IDs with associated test methods
- Method numbers and summary
- Chain-of-custody documentation including shipping documents
- Sample receipt checklist
- Telephone conversation and email records for the project
- Dates of sample extraction and analysis
- Sample results for all neat and diluted runs, including units, matrix, qualifiers, dilution factors and percent solids
- Sample preparation information, including batch numbers
- Raw data for initial and continuing calibrations
- GC/MS tuning results
- Run logs
- Method detection limits and method/practical quantitation limits
- Results, true values, and/or acceptance limits for MS/MSDs, method or preparation/calibration blanks, LCSs, internal standard areas, surrogate spikes, interference checks, and serial dilutions
- Raw data for samples and laboratory QC samples, including labeled and dated chromatograms/ spectra

The case narrative will include the client name, project name and number, date of issuance, and a discussion of any deviations from analytical strategy (e.g., samples received but not analyzed), sample receipt issues (e.g., incorrect preservatives, air bubbles in VOC vials), missed holding times, definition of data qualifiers or flags, identification of manually integrated data, technical problems, and QC failures or nonconformances and associated corrective actions. The report will be signed by the Laboratory Project Manager.

Once the electronic data files have been received from the laboratory, the data will be electronically reviewed using qualified personnel to check project data quality. All electronic data submitted by the contract laboratory is required to be error-free, and in complete agreement with the hardcopy data. The electronic CD of the data must be submitted with a transmittal letter from the laboratory that certifies that the file is in agreement with hardcopy data reports and has been found to be free of errors.

8.0 QUALITY CONTROL

8.1 FIELD QUALITY CONTROL

The quality control (QC) measurements for field measurements will be limited to the calibrations described in Section 5.1.2. Field QC samples will be collected during groundwater sampling to assess the accuracy and precision of the laboratory data. These samples include trip blanks, equipment blanks, field duplicates, and MS/MSDs. The collection of QC samples and the acceptance criteria for these samples is described below.

Trip blanks – Trip blanks will be included with each shipment of VOC samples. Trip blanks associated with aqueous VOC samples will originate in the laboratory and will be prepared by filling two 40-mL VOA vials with laboratory deionized water and preservative and sealing the vials with septum-lined caps (allowing no headspace). Trip blanks associated with soil samples will contain deionized water for low level analyses. Trip blanks will accompany the sample bottles to the site and will remain (unopened) in the shipping container until the sample bottles are received back at the laboratory. Analytes in the trip blanks, if detected, should be <1/2 the laboratory reporting limit.

Equipment (field or rinsate) blanks – Equipment blanks will be prepared by routing analyte-free water (provided by the laboratory) through or over non-dedicated sampling equipment after equipment decontamination and before field sample collection. Equipment blanks will be collected for samples collected with non-dedicated equipment (at a frequency of one per day) and will be analyzed for the same compound list as the primary samples. Analytes in the equipment blanks, if detected, should be <1/2 the laboratory reporting limit.

Field duplicates – Field duplicates (replicates for metals analysis) will be collected at a frequency of one field duplicate for every 20 or less samples of each matrix (solid or liquid) submitted for analyses. Sample containers for aqueous field duplicates will be filled consecutively. Field duplicate relative percent differences (RPDs) are considered acceptable if they are <30% for aqueous samples and <50% for solid samples.

MS/MSDs – MS/MSD samples and Replicates (metals) will be collected at a frequency of one for every 20 or less samples of each matrix submitted for analyses. For those samples designated as MS/MSDs, sufficient additional volume will be provided as required for analysis. Acceptance criteria for the percent recoveries of spiked compounds and RPDs for the laboratory duplicate analyses are 40% for Method 524.2.

8.2 LABORATORY QUALITY CONTROL

The analytical laboratory has a QC program in place to ensure the reliability and validity of the analysis performed at the laboratory. All analytical procedures are documented in writing as SOPs and each SOP includes the minimum requirements for the procedure. Additional specifics regarding quality control are also provided in Section 12. In general the QC requirements include the following:

- Blanks (method, reagent/preparation, instrument)
- MS/MSDs (replicates for metals)
- Surrogate spikes
- Laboratory control standards (LCSs)
- Internal standard areas and retention times (GC/MS analysis)
- Interference checks (metals analysis)
- Serial dilutions (metals analysis)

9.0 SAMPLE DOCUMENTATION, PACKAGING AND CUSTODY REQUIREMENTS

This section describes the sample collection protocols required to satisfy the data quality objectives for this field effort.

9.1 SAMPLE COLLECTION DOCUMENTATION

During field work, field logbooks will be maintained by the field team. Logbooks and chain-of-custody (COC) records will be employed to maintain a comprehensive record of sample collection, transfer between personnel, shipment, and receipt by the laboratory.

9.2 FIELD NOTES

Bound field logbooks will be used to document all field activities and will contain sufficient data and information to reconstruct field activities for a specific day. Field notes will be recorded pursuant to SOP-JCO-034, Use of Field Log books. Pages in the logbook will be bound and sequentially numbered. All entries will be in indelible ink. At the end of the day, the last page will be initialed and dated by the author(s) and a line drawn through the remainder of the page. At the end of the day, the daily log will contain, at a minimum, the following information regarding the project sampling operations:

- Site name and location;
- Date and time the field work started and finished;
- Names of sampling personnel;
- Location and description of the samples and sample sites including site sketches or diagrams;
- Sample identification and description;
- Date, time and COC number for each sample was collected;
- Any deviations from this document;
- Meteorological conditions and changes in these conditions;
- Record of any field measurements made (unless otherwise recorded on applicable field sheets);
- Calibration and decontamination procedures and/or adjustments (unless otherwise recorded on applicable field sheets);
- Packaging information (unless recorded on COC); and
- Sample destination (unless recorded on COC).

Errors on field documents, including logbooks, will be corrected by drawing a line through the error and entering the correct information. All corrections will be initialed and dated.

9.3 SAMPLE PACKAGING AND SHIPPING

Samples for laboratory analysis will be placed in containers and preserved as described in Table 9-1. The samples will be packaged for shipment in protective media, i.e., bubble-wrap, and individual sealed plastic bags, etc., and chilled by adding ice or freezer packs in each cooler, along with a temperature blank. Custody seals will be attached to the outside of the shipping container in such a manner that the seal must be broken to allow access to the container. Refer to JCO SOP "Chain-of-Custody Procedures" as provided in Appendix 1 for a detailed description of custody procedures.

Table 9-1
Containers, Preservatives, and Holding Times

Parameter	Container	Preservative	Holding Time*
Groundwater Parameters			
VOCs 524.2	3 x 40-ml VOA vials w/septa	HCl to pH<2; Cool to 4ºC	14 days
Methane/Ethane/Ethene RSK-175	3 x 40-ml VOA vials w/septa	H_2SO_4 to pH <2; Cool to 4ºC	14 days
Sulfate 375.4	250 ml plastic	Cool to 4ºC	28 days
Sulfide 376.1	250 ml plastic	Cool to 4ºC	7 days
Nitrate/Nitrite 353.2	500 ml plastic	Cool to 4ºC	48 hours
Ammonia 350.2	250 ml plastic	H_2SO_4 to pH <2; Cool to 4ºC	28 days
Total Phosphorous 365.2			

***Advisory holding times**

All samples sent to the laboratory for analysis will be hand delivered or shipped overnight via commercial carrier. The carrier air-bill number will be included on the COC in the box on the lower right labeled: Shipper ID#. Nitrate, nitrite, sulfate and sulfide samples will be shipped to STL Chicago. All other laboratory samples will be sent to STL Burlington.

STL Burlington
30 Community Drive, Suite 11
South Burlington, VT 05403
Telephone: 802-660-1990

STL Chicago
417 Bond Street
University Park, IL 60466
Telephone: 708-534-5200

The following checklist should be checked prior to shipping.

SHIPPING CONTAINER CHECKLIST SUMMARY

- Is the project clearly identified on the Chain-of Custody (official project name, project location, project phase)?
- Are all enclosed sample containers clearly labeled with waterproof (permanent) ink and enclosed in a plastic bag?
- Are the desired analyses indicated on the bottle labels and chain-of-custody?
- Are the sample labels complete, including method numbers for both preparatory and analysis procedures?
- Does the information on the Chain-of-Custody match the sample containers labels?
- Is the Chain-of-Custody in a plastic bag and attached it to the inside of the cooler lid?
- Have the samples been properly preserved (acid or base and cooling to 4^{O} C$\pm$ 2 ^{O}C)?
- Is there a Contractor point of contact including name and phone number clearly shown on the Chain-of-Custody?
- Is there sufficient ice (double bagged in zip-locks) or "blue ice" in the cooler? It is recommended that the samples be placed on ice as soon as possible after sampling and repacked on new ice in the shipping cooler.

9.4 CUSTODY PROCEDURES

Custody is one of several factors that are necessary for the admissibility of environmental data as evidence in a court of law. Custody procedures help to satisfy the two major requirements for admissibility: relevance and authenticity. Sample custody is addressed in two parts: 1) field sample collection; and 2) laboratory analysis. A sample is considered to be under a person's custody if:

- the item is in the actual possession of a person;
- the item is in the view of the person after being in actual possession of the person;
- the item was in the actual physical possession of the person but is locked up to prevent tampering;
- the item is in a designated and identified secure area.

9.4.1 *Field Custody Procedures*

The field sampler is personally responsible for the care and custody of the samples until they are transferred or dispatched properly. Field procedures have been designed such that as few people as possible will handle the samples.

Sample containers will be identified by the use of sample labels with sample numbers, sampling locations, date/time of collection, and type of analysis. Sample labels will be completed for each sample using waterproof ink unless prohibited by weather conditions. For example, a logbook notation would explain that a pencil was used to fill out the sample tag because the pen would not function in rain or freezing weather.

Samples will be accompanied by a properly completed COC form. The sample numbers and locations will be listed on the COC form. When transferring the possession of samples, the individuals relinquishing and receiving will sign, date, and note the time on the record. This record documents the transfer of custody of samples from the sampler to another person, to the laboratory, or to/from a secure storage location. An example COC form is presented in Appendix 4, SOP-JCO-007.

Sample shipments will be accompanied by the COC record identifying the contents. The original record will accompany the shipment, and the pink and yellow copies will be retained by the sampler and placed in the sampler and project files.

Samples will be packaged on ice at $\leq$4°C for shipment and dispatched to the laboratory for analysis, with a separate signed custody record enclosed in and secured to the inside top of each sample box or cooler. Shipping containers will be locked and secured with strapping tape and custody seals for shipment to the laboratory. The custody seals will be covered with clear plastic tape after being signed by field personnel. The cooler will be strapped shut with strapping tape in at least two locations.

If the samples are sent by common carrier, the waybill will be used. Waybills will be retained as part of the permanent documentation. Commercial carriers are not required to sign off on the custody forms since the custody forms will be sealed inside the sample cooler and the custody seals will remain intact. Commercial carrier air-bill numbers will be included on the COC in the box on the lower right labeled: Shipper ID#.

Samples are expected to be transported to the laboratory within 24 hours of the time the samples are collected in the field. All efforts will be made to ship the samples on the same day as collection, but in some instances it may not be possible due to sample collection and sample delivery schedule conflicts. Samples will be hand delivered, shipped by overnight commercial carrier or will be transported by same-day courier.

9.4.2 *Laboratory Custody Procedures*

Samples will be received and logged in by a designated sample custodian or his/her designee. Upon sample receipt, the sample custodian will:

- Examine the shipping containers to verify that the custody tape is intact,
- Examine sample containers for damage,
- Determine if the temperature required for the requested testing program has been maintained during shipment BY MEASURING THE TEMPERATURE BLANK and document the temperature on the COC form,
- Compare samples received against those listed on the COC,
- Verify that sample holding times have not been exceeded,
- Examine shipping records for accuracy and completeness,
- Determine sample pH (if applicable) and record on the COC,
- Sign and date the COC immediately (if shipment is accepted) and attach the waybill,
- Note any problems associated with the coolers and/or samples on the cooler receipt form and notify the Laboratory Project Manager, who will be responsible for contacting the client,
- Attach laboratory sample container labels with unique laboratory identification and test,
- Place the samples in the proper laboratory storage.

Following receipt, samples will be logged in according to the following procedure:

- The samples will be entered into the laboratory information management system (LIMS). At a minimum, the following information will be entered: project name or identification, unique sample numbers (both client and internal laboratory), type of sample, required tests, date and time of laboratory receipt of samples, and field ID provided by field personnel.
- The appropriate laboratory personnel will be notified of sample arrival.
- The completed chain-of-custody, waybills, and any additional documentation will be placed in the project file.

Specific details of laboratory custody procedures for sample receiving, sample identification, sample control, and record retention are described in the laboratory SOPs.

10.0 INVESTIGATION DERIVED WASTE

10.1 SOLID WASTE

Solid investigation-derived waste (IDW) for this program is anticipated to include sampling equipment and personal protective equipment (PPE). The plastic, glass, and personal protective equipment IDW will be double bagged in plastic trash bags and placed into a dumpster for eventual disposal at a lined landfill.

10.2 LIQUID WASTE

Liquid IDW for this program is anticipated to include purge water from sampling activities, equipment and field rinse water, and decontamination water. Based on analytical data collected on the project to date, and the NYSDEC prior approval of the Weston Solution Sampling and Analysis Plan and IDW disposal practices, all investigation-derived waste (IDW) will be treated as non-hazardous and disposed of accordingly. Previous results show that purge water produced by the six wells sampled will have VOC results below both federal and state MCLs. Purge water from the monitoring wells will be discharged to an impervious surface (asphalt, concrete, plastic sheets, etc.) to facilitate evaporation/volatilization. Water purged from the residential supply wells taken at the faucet or spigot will be allowed to drain normally through the associated plumbing.

11.0 CORRECTIVE ACTION

11.1 FIELD CORRECTIVE ACTION

Corrective action in the field may be needed when the sample network is changed (i.e., more/less samples, sampling locations other than those specified in the SAP, etc.), or when sampling procedures and/or field analytical procedures require modification, etc. due to unexpected conditions. The field team may identify the need for corrective action. The FTM will approve the corrective action and notify the PM. The PM, in consultation with the QAO, will approve the corrective measure. The FTM will ensure that the corrective measure is implemented by the field team.

Corrective actions will be implemented and documented in the field record book. Documentation will include:

- A description of the circumstances that initiated the corrective action,
- The action taken in response,
- The final resolution, and
- Any necessary approvals.

No staff member will initiate corrective action without prior communication of findings through the proper channels.

11.2 LABORATORY CORRECTIVE ACTION

Corrective action in the laboratory may occur prior to, during, and after initial analyses. A number of conditions such as broken sample containers, multiple phases, low/high pH readings, and potentially high concentration samples may be identified during sample log-in or analysis. Following consultation with laboratory analysts and supervisory personnel, it may be necessary for the Laboratory QA Coordinator to approve the implementation of corrective action. If the nonconformance causes project objectives not to be achieved, the QAO will be notified.

These corrective actions are performed prior to release of the data from the laboratory. The corrective action will be documented in both the laboratory's corrective action files, and in the narrative data report sent from the laboratory to the QAO. If the corrective action does not rectify

the situation, the laboratory will contact the QAO, who will determine the action to be taken and inform the appropriate personnel.

12.0 DATA VALIDATION/DATA USABILITY

A completeness goal of 95% shall be used for the project. That is, more than 95% of the data must be usable (not qualified as "rejected" during the data review) with the exception of serial dilutions where the result for one dilution is rejected and replaced by that of another.

Acceptable limits for laboratory quality control tests are described in the Department of Defense (DoD) Quality Systems Manual – Version 3 Final. Laboratory specific standard operating procedures (SOPs) are also included in Appendix 3. Table 4-2 provides the PQL/MDL requirements for the Method 524.2 target analytes. Table 12-1 provides a summary of Method 524.2 quality control limits, which are also provided on page 18 of the STL SOP (including corrective actions) in Appendix 3. Corrective actions are provided in Table 1 of the attached laboratory SOP.

Table 12-1
Method 524.2 Quality Control Limits

Quality Control Check	Minimum Frequency	Acceptance Criteria
Check mass spectral ion intensities using BFB	Prior to initial calibration and calibration verification	Response Factor (RF) relative standard deviation (RSD) less than or equal 20%
Five point calibration for all analytes of interest	Initial calibration prior to sample analysis	RF for all analytes of interest within 30% (%D) of the average initial multi-point RF
Internal Standard (IS)	Once every 12 hours, prior to sample analysis	Retention time within 30 seconds and extracted ion current profile (EICP) area within 50% to 100% of previous 12-hour calibration for each IS.
Method Blank	Once per 12-hour window	No analytes of interest detected above practical quantitation limit (PQL)
Lab fortified blank (LFB) analytes spiked at 1 ppb	One LFB per 12-hour window	Reported concentrations within 70-130% of actual values
Surrogate Spike	Every sample, control standard and method blank	Reported concentrations within statistically derived limits
Lab fortified sample matrix (LFM)	Only if IS acceptance criteria are not met, or if matrix effects are observed in samples	Reported concentrations within 70-130% of actual values
Method Detection Limit (MDL) Study	Once per year	PQL of at least three times the MDL
Demonstrate acceptable P & A using four replicate analyses of a QC check standard	One time per analyst initially, and annually thereafter	All recoveries within 70-130% of actual values

All data packages will be reviewed to confirm compliance with the comprehensive data package requirements outlined in the *Chemical Quality Assurance for HTRW Projects*, EM 200-1-6, Chapter 2, Section 2-1, Item (c). Although EPA Contract Laboratory Program (CLP)-type data validation will not be performed for this project, a comprehensive data package allows complete data reconstruction in the future, if required. At a minimum, the laboratory data package must include the following information:

- A cover sheet with laboratory name and location, project name, and statement of data authenticity and official signature of release;
- Table of Contents;
- A case narrative describing the procedures performed by the laboratory, any deviations from the methods, problems encountered during sample receiving and analysis, definition of all data qualifiers or flags, and any other factors that could affect the sample results;
- A cross-reference between the field sample identification numbers and the laboratory sample identification numbers;
- Tabulated sample results with proper field and laboratory sample identification numbers; analytical method numbers; dates of collection, receiving, extraction/preparation, and analyses; dilution factors; matrix; sample weight/volume used for sample preparation/analysis; final extract volume; units specified by each methods; and detection limits for compounds/analytes reported with ND and/or less than;
- Raw data for samples, standards, and QC analyses in the form of instrument printouts, chromatograms, strip chart recordings, and quantitation reports;
- Spectra of positively identified compounds by Gas Chromatography/Mass Spectrometry (GC/MS);
- Tabulated results of QC analyses with respective acceptance criteria for initial calibration, continuing calibration, method blank, surrogate spike recovery, MS/MSD, laboratory control samples (LCS) (if any) and laboratory duplicate (if any), and internal standard performance (Gas Chromatography/Mass Spectrometry [GC/MS] only); and
- Copies of sample documentation such as chain-of-custody and lab log-in sheets, and correspondences between Weston and the contract laboratory.

A limited data validation will be conducted on the sample analysis performed by the contract laboratory. The data validation will consist of the following activities:

- Review of chain-of-custody documents to verify sample identities;
- Review of sample log-in documents to identify any potential problems with custody seals, container integrity, sample preservation, labeling, etc;
- Review of trip blank data to identify any potential problems with sample container contamination, preservative contamination, laboratory reagent water contamination, or cross-contamination between samples during transport;
- Review of method blank data to determine the presence of any sources of contamination in the analytical process;
- Review of the MS data to evaluate the potential for matrix effects as a measure of analytical accuracy. MS recoveries will be compared against laboratory acceptance criteria to determine if they are within or outside of warning and control limits for percent recoveries;
- Review of MS/MSD data to evaluate sample homogeneity and as a measure of analytical precision. MS/MSD data will be compared to laboratory acceptance criteria for the maximum relative percent difference (RPD);
- Review of blank spike (BS) data (if available) as a measure of analytical accuracy. BS recoveries will be compared against laboratory acceptance criteria to determine if they are within or outside of warning and control limits for percent recoveries;
- Review of blank spike and blank spike duplicate (BS/BSD) data (if available) as a measure of analytical precision. BS/BSD data will be compared to laboratory acceptance criteria for the maximum RPD;
- Review of standard reference material (SRM) or LCS data (if available) as a measure of analytical accuracy. SRM and LCS data will be compared to the certified acceptable ranges of analytical values;
- Review of sample and sample duplicate data (if available) as a measure of sample homogeneity and as a measure of analytical precision. Sample and sample duplicate data will be compared against the laboratory acceptance criteria for the maximum RPD;
- Review of surrogate recovery data to access extraction efficiency (if applicable) of sample introduction, and possible loss during cleanup activities. Surrogate recoveries will be compared to laboratory acceptance criteria to determine if they are within or outside of acceptable limits;
- Review of sample data, extraction/digestion dates (if applicable), and analysis dates to determine if maximum holding times were met or exceeded; and

- Determine completeness as a percentage of measurements made which are judged to be valid measurements compared to the total number of measurements planned.

Review of initial calibration results will be conducted in terms of percent standard deviation (%RSD) to ensure acceptable instrument linearity has been achieved before sample analysis. Review of continuing calibration results will be conducted in terms of percent difference (%D) of compound response factors between initial and continuing calibrations to verify the validity of the initial calibration.

12.1 DATA REVIEW

12.1.1 Field Data

Field data will be reviewed by the FTM to verify that the records are complete, accurate, and legible and to verify that the sampling procedures are in accordance with the protocols specified in this SAP.

12.1.2 Internal Laboratory Review

Prior to the release of any data from the laboratory, the data will be reviewed and approved by laboratory personnel. The review will consist of a tiered approach that will include reviews by the person performing the work, by a qualified peer, and by supervisory and/or QA personnel.

12.2 VERIFICATION AND VALIDATION METHODS

12.2.1 Field data verification

Field records will be reviewed by the FTM to ensure that:

- Logbooks and standardized forms have been filled out completely and that the information recorded accurately reflects the activities that were performed.
- Records are legible and in accordance with good recordkeeping practices, i.e., entries are signed and dated, data are not obliterated, changes are initialed, dated, and explained.
- Sample collection, handling, preservation, and storage procedures were conducted in accordance with this SAP and that any deviations were documented and approved by the appropriate personnel.

12.2.2 Laboratory Data Verification

Prior to being released as final, laboratory data will proceed through a tiered review process. Data verification starts with the analyst who performs a 100 percent review of the data to ensure the work was done correctly the first time. The data reduction and initial verification process must ensure that:

- Sample preparation and analysis information is correct and complete,
- Analytical results are correct and complete,
- The appropriate SOPs have been followed and are identified in the project records,
- Proper documentation procedures have been followed, and
- All nonconformances have been documented.

Following the completion of the initial verification by the analyst performing the data reduction, a systematic check of the data will be performed by an experienced peer or supervisor. This check will be performed to ensure that initial review has been completed correctly and thoroughly and will include a review of:

- Adherence to the requested analytical method SOP,
- Correct interpretation of chromatograms, mass spectra, etc.,
- Correctness of numerical input when computer programs are used (checked randomly),
- Correct identification and quantification of constituents with appropriate qualifiers,
- Numerical correctness of calculations and formulas (checked randomly)
- Acceptability of QC data,
- Documentation that instruments were operating according to method specifications (calibrations, performance checks, etc.),
- Documentation of dilution factors, standard concentrations, etc.,
- Sample holding time assessment.

A third-level review will be performed by the Laboratory Project Manager before results are submitted to clients. This review serves to verify the completeness of the data report and to ensure that project requirements are met for the analyses performed. A narrative to accompany the final report will be prepared by the Laboratory Project Manager.

13.0 REFERENCES

NYS DEC, 1989; Disposal of Contaminated Groundwater During Remedial Investigations, NYSDEC Division of Hazardous Waste Remediation TAGM, 30 November 1989.

NYS DEC, 2002; Draft Der-10 Technical Guidance for Site Investigation and Remediation, NYSDEC
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USACE, 2004, Engineer Regulation (ER) 200-3-1, Formerly Used Defense Sites Program Policy.

USACE, 2007, Statement of Work for Groundwater monitoring in support of Site Closeout at Former Atlas Site S-11, Ellenburg, New York; February 2007, revised March, 2007

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USEPA Region I, 1996, Low Stress Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells, SOP #GW0001, July 30, 1996, Revision 2.

USEPA, 1998; Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water, U.S. Environmental Protection Agency, EPA/600/R-98/128, September 1998.

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Weston, 2006a; Draft Proposed Long-Term Monitoring Sampling and Analysis Plan, Former Atlas Site S-11, Ellenburg, New York, Weston Solutions, Inc., May 8, 2006.

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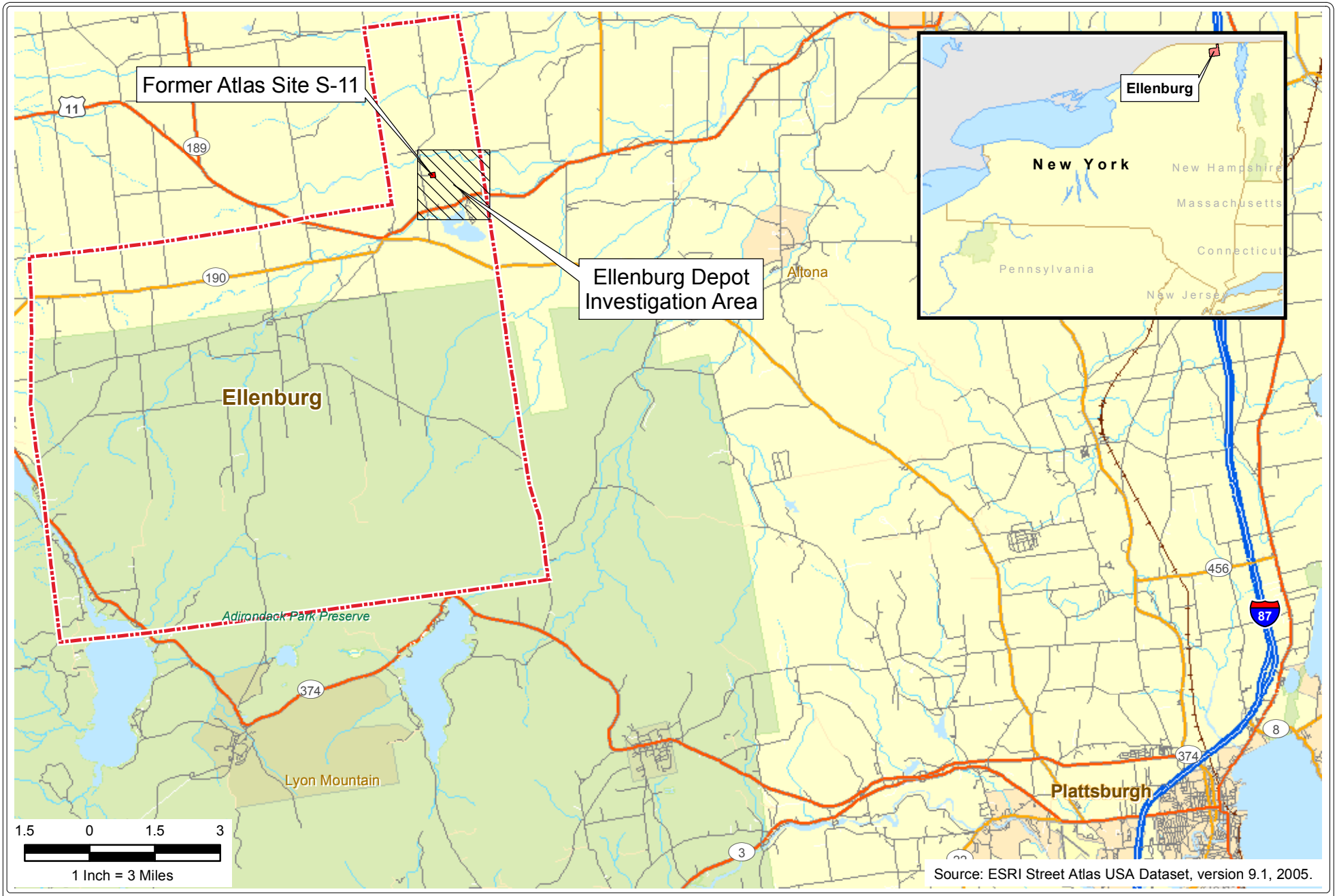
FIGURES

P:\Atlas Missle\Atlas_GIS\MXD\2006_09_Rnd7_Report\03839_Site_Loc_Map.mxd



WESTON SOLUTIONS	PROJECT: FORMER ATLAS SITE S-11	TITLE: SITE LOCATION MAP
DATE: SEPTEMBER 2006	CLIENT NAME: U.S. ARMY CORP OF ENGINEERS	
FIGURE #: **1-1**		

N

MW-05
210'

MISSILE BASE R.O.W.

FORMER ATLAS
SITE S-11

MW-01
200'

BULL RUN ROAD

MW-3

MW-03
130'

MW-08
115'

MW-02
200'

MW-04
105'

MW-06
55'

MW-01
65'

PW-24

PW-118

PW-80

PW-35

PW-68

CANAAN ROAD

TOWN OF ELLENBURG

TOWN OF ALTONA

STATION HILL ROAD

ROUTE 11

LAKE ROXANNE ROAD

GREAT CHAZY RIVER

PLANK ROAD

KEY

- LONG TERM GROUNDWATER MONITORING LOCATION
- POTABLE WELL LOCATION
- MONITORING WELL LOCATION
- BUILDING / STRUCTURE
- SURFACE WATER
- VEGETATION
- FENCELINE

0 150 300 600
SCALE IN FEET

SOURCE: WESTON SOLUTIONS, INC. DRAWING DATED DECEMBER 2006.

DRAFT

Weston.dwg

FIGURE 1-2
PLANNED WORK AREAS
FORMER ATLAS SITE S-11
ELLENBURG, NEW YORK

THE JOHNSON COMPANY, INC.
Environmental Sciences and Engineering
100 STATE STREET MONTPELIER, VT 05602

DATE: 4/18/07 DRAWN BY: TJK PROJECT: 1-2128-5 SCALE: 1"=600'

APPENDIX 1

STANDARD OPERATING PROCEDURES

AND SITE SPECIFIC METHODS

SOP-JCO-007	Chain of Custody
SOP-JCO-009	Water Level Measurement
SSM-JCO-027	Decontamination of Equipment
SOP-JCO-034	Use of Field Log Books
SOP-JCO-041	Calibration and Operation of PID
SSM-JCO-053	Low Stress Groundwater Sampling
SSM-JCO-055	Calibration and Use of YSI Model 6210XL, The DRT-15CE and Lamotte 2020 Turbidimeters, the HACH DR890 Colorimeter, and CHEMetrics Field Analysis

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Standard Operating Procedure For Chain-of-Custody Records

INTRODUCTION

The chain-of-custody record allows for the tracking of possession and handling of individual samples from the time of field collection through laboratory analysis. All samples released from field operations shall be accompanied by a Chain-of-Custody Form (Attachment JCO-007-1). This is done to insure the legal integrity of the sample materials collected. Every effort shall be made to keep as few people as possible in the chain of sample possession.

PROCEDURE

1. A completed Chain-of-Custody Form shall accompany each set of samples released from the study site. The Chain-of-Custody Form for all samples shall include the following information:

   a. Signature of Sampler
   b. Client/Project name
   c. Project Location
   d. Field Logbook Number (e.g. page no. in field book)
   e. Sample Number, Identification
   f. Date and time of sample collection
   g. Type of Sample (Air, water, soil, etc.)
   h. Analysis requested
   i. Preservative Added (Remarks section)
   j. Source of the Sample (Remarks section)
   k. Chain-of-Custody Tape Number
   l. Inclusive Dates of Possession
   m. Signatures of persons involved in chain of possession
   n. Name of person the analytical results are to the attention of (in lower right corner of the form).

2. The Chain-of-Custody Form is designed in quadruplicate. Each of the individual four sheets is a different color. Along the bottom of each sheet are the instructions describing who gets which copy. These instructions are as follows:

White Copy:	Original sheet to accompany sample to the lab and returned to The Johnson Company.
Yellow Copy:	Laboratory Copy
Pink Copy:	Transporter Copy (optional)
Orange Copy:	Sampler Copy

Therefore, after the Chain-of-Custody Form has been completely filled out, the sampler signs the initial "Relinquished by" along with date and time and obtains the signature of the next person (i.e. transporter) in the chain-of-custody (in the initial "Received by" box along with date and time. The sampler then tears off the back (orange) copy for his records. Then the transporter delivers the samples to the analytical lab, he signs the second "Relinquished by" box along with date and time, and a laboratory representative signs the second "Received by" box along with the date and time. At this point, the transporter has the option of retaining the Pink copy for his records.

Instructions shall be given to the laboratory regarding their responsibilities in returning the top sheet (white copy) to The Johnson Company with the lab results. This sheet contains all sample information and original signatures. The lab should retain the yellow copy for their records.

If the sampler his- or herself delivers the samples to the laboratory, then the sampler should make certain the receiving party at the lab signs in the proper space, i.e., "Received for Laboratory".

3. The Chain-of-Custody form shall be completed in legible hand writing with indelible ink, with all the appropriate information completed. Once completed, the form is either:

   a. placed in a plastic-wrap and included with the samples in the cooler, or;

   b. fixed in an envelope taped securely in top of the cooler or plastic packing slip container (if available). This method allows for signatures to be included with each transfer of custody. This method is mandatory in the event a non-commercial courier is utilized to transport samples.

4. The sample container shall be sealed with chain-of-custody tape, containing the designation, date, and sampler's signature. The custody tape is especially important when shipping the container via overnight courier such as Federal Express and United Parcel Service.

Revision Author: Tammy R Bowey Date: 3/13/96
Scientist, Engineer or Technician

Reviewed: [signature] Date: 3/13/96
Director, Quality Assurance Unit

Approved: [signature] Date: 3/13/96
Vice President

JCOSOP.007

ATTACHMENT SOP-JCO-007-1

Chain-of-Custody Form (following page)

CHAIN OF CUSTODY RECORD

8464

Client / Project Name	Project Location	ANALYZES
Project No.	Field Logbook No.	
Sampler: (*Signature*)	Chain of Custody Tape No.	

Sample No. / Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS

Relinquished by: (*Signature*)	Date	Time	Received by: (*Signature*)	Date	Time
Relinquished by: (*Signature*)	Date	Time	Received for Laboratory: (*Signature*)	Date	Time
Sample Disposal Method:	Disposed of by: (*Signature*)			Date	Time

SAMPLE COLLECTOR

100 State Street, Suite 600
Montpelier, VT 05602
(802) 229-4600
Fax (802) 229-5876

THE JOHNSON COMPANY, INC.
Environmental Sciences and Engineering

ANALYTICAL LABORATORY

Shipper ID #

WHITE - To accompany sample to the lab and returned to the Johnson Co. YELLOW - Lab copy PINK - Transporter copy GOLD - Sampler copy

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Standard Operating Procedure For Water Level Measurement

PROCEDURE

1. An elevation from which to measure the depth to water will be established on a permanent reference point. In the case of observation and monitoring wells, this point will be a permanent mark on the top of the well casing. Specifically, in the case of locking well guards set over the well, it is important that the reference mark be set on the well casing itself and not the top of the well guard.

2. The measurement begins by first unlocking the well guard if one is present, then removing the cap of the well. Care must be taken not to set the cap on the ground.

3. When electrical water markers are used, an electrical probe connected to the graduated wire is lowered down the well casing. A light turning on or a meter deflection indicates that the probe tip has touched the water. When this indication occurs, the reading is taken by observing and noting the length of graduated wire between the reference mark and water level probe tip.

   If non-aqueous phase liquid (NAPL) is known or expected to be present, the measurements shall be made with an interface probe. The probe is lowered slowly into the well until a liquid is encountered. The probe signifies a low conductance liquid (NAPL) with a continuous tone. After noting this reading, the probe is then slowly lowered deeper into the well to determine the position of the NAPL/water interface. The presence of a high conductance fluid (water) is indicated by an intermittent tone, and this reading is noted.

4. Measurements should be recorded on a field log book, or if applicable, Form JCO-HYDRO-005 (Attachment SOP-JCO-009-1). Additional data to be recorded include the well or station identification; the time of measurement in 24 hour mode; and any pertinent comments regarding conditions of that measurement. The depth to NAPL and to water shall be recorded to the closest 1/100 foot. The measurements should be clearly recorded in columns labeled "water" and "NAPL". If either fluid is absent a dash (-) should be placed in the appropriate column. If the well location is not a NAPL site, "Not Applicable" shall be lettered vertically in the NAPL column.

5. The probe and tape should be wiped with a rag to remove any NAPL following the measurement. The probe and tape should then be washed with Liquinox or similar lab-grade soap and thoroughly rinsed with distilled water before use in another well.

6. When water level measurements are being taken in monitoring wells, the probe tip shall be rinsed with deionized water and dried between wells to prevent cross contamination.

7. The sequence of water level measurements shall be from least likely to most likely contaminated sampling points in order to reduce the potential for cross contamination.

8. Following sampling, the cap is then set back on the well casing, and the locking well guard re-locked (if applicable).

Author: Tammy R Bowen Date: 12/17/99
Scientist, Engineer or Technician

Reviewed: [signature] Date: 1/19/00
Technical Reviewer

Approved: [signature] Date: 1/18/00
Officer

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FORM JCO-HYDRO-005 (Revised 11/90)

Job:__________________________

Measured by: Date:

WATER LEVEL LOG

Well #	Depth to NAPL (ft)	Depth to Water (ft)	Time (24 hour mode)	Comments

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Site Specific Method For
Decontamination of Field Equipment

1.0 INTRODUCTION

Decontamination procedures are performed as a quality assurance measure and a safety precaution. The overall integrity of the sampling program is maintained, in part, through a conscientious decontamination program. The procedure prevents cross-contamination between sample stations and helps maintain a clean working environment for the safety of all field personnel. An underlying procedure that will help minimize cross-contamination is to always sample background or uncontaminated stations first (if known).

Decontamination is mainly achieved by rinsing with liquids which may include as appropriate: detergent solutions, tap water, deionized water and Citra-solv. Equipment will be allowed to air dry after being cleaned or may be wiped dry with chemical-free cloths or paper towels.

Decontamination shall in most cases be accomplished at each sampling site, between collection points. Waste produced by the decontamination procedures may require collection and proper disposal.

1.1 General Considerations

1.1.1 Planning: When planning fieldwork, always create an investigation or sampling sequence that starts with the least contaminated location and proceeds through progressively more contaminated locations to the most contaminated location. In the case of surface water sampling, sample collection should proceed in an upstream direction. In the absence of data to indicate the degree of contamination, the judgment of the person planning the fieldwork will dictate the sequence of investigation or sampling, in accord with this guidance.

1.1.2 Clothing: Persons performing decontamination procedures shall wear the same type of personal protective equipment during decontamination as was worn when the fieldwork was performed. Persons performing decontamination are always required to wear chemical-resistant gloves.

1.1.3 Location: Decontamination procedures are generally to be performed at the site, and preferably at the location of fieldwork, to minimize the spread of contaminants. When numerous investigation or sample locations are in very close proximity, as in the case with well clusters, decontamination stations are acceptable and efficient. Clean plastic sheets should be placed on the ground at the decontamination site to keep the site clean and to minimize the creation of mud.

1.1.4 Collection of Waste Water: Site-specific plans, protocols, or specifications may require collection of all fluids used for decontamination of field equipment. Field workers should be aware of this requirement prior to beginning fieldwork and should make ample preparation for collection and storage of the fluids used if this requirement is applicable.

2.0 PROCEDURE

2.1 Specific Procedures for Hand-held Field Equipment

The following procedure is to be used to decontaminate hand held field equipment including: hand augers, Shelby tubes, split-spoon samplers, bailers, purge pumps, well probes, shovels, trowels, plastic tubing, or other soil or water contact equipment.

2.1.1 List of Required Equipment and Supplies: Field managers are advised to supply the following materials in advance of fieldwork. The absence of required decontamination equipment and supplies is not an acceptable deviation from this procedure, and may result in unusable or limited use of sample results.

Ample Quantities of Deionized water (1 gallon per procedure)
Clean 5-gallon buckets (3)
Liquinox Laboratory-Grade Soap or equivalent brand
Isopropyl Alcohol
Several large clean plastic sheets or drop cloth or plastic wading pool
Clean hand-held brushes
Chemical Resistant Gloves appropriate to site contaminants
Sample Bottles for Field Blank Collection
Hose or Pressure Spray Tank for large devices
Citrus-based solvent such as Citra-solv (if gross NAPL or organic solids contamination)
Paper towels
Safety glasses or eye protection

If collection of wastewater is required:
Shovel (to create berms for plastic sheeting)
55-Gallon DOT Barrels
Funnel
Pumps and hose

2.1.2 Remove Solids and Gross Contamination: Removal of mud, sludge, vegetation or other solids from the equipment must be done prior to decontamination. Removal of solids is most easily done using a brush and ample quantities of water. Distilled or deionized water is not required for this step. A bucket can be used to hold small devices during this step, while larger items, such as hand augers, can be cleaned over plastic with a hose or pressurized spray tank, if available.

Restrict the use of Citra-solv to those instances in which gross contamination, such as NAPL or organic-based solids, is present. On those occasions, Citra-solv may be used to dissolve the contaminant, followed by a triple rinse with tap water to remove the Citra-solv.

2.1.3 Remove Trace Contamination: Removal of trace amounts of contamination is done using a solution composed of laboratory grade soap, such as Liquinox, and water. This solution is mixed in a bucket. Small field devices can be immersed in the bucket, while larger field devices, such as hand augers, must be cleaned with a brush and hose or pressurized spray tank.

2.1.4 Remove Soap Solution: The residual soap solution is removed following scrubbing by rinsing the device with tap water. Small field devices can be immersed in a bucket of tap water provided suds are not present from the previous use. Larger devices must be rinsed with a hose or pressurized spray tank. The volume of water used should be at least 5 times the volume of soap solution used in the previous step.

2.1.5 Final Rinse: All field equipment is rinsed with deionized or distilled water to remove any residual soap or tap water. This process is repeated with fresh deionized or distilled water at least twice.

2.1.6 Field Drying: The decontaminated tool or instrument should be allowed to air dry prior to use. In weather conditions where this is not possible a hot air blower may be used to dry the field equipment.

2.1.7 Collection of Field Blanks: Field blanks are to be collected to measure the effectiveness of field decontamination procedures. Site-specific plans or specifications should be consulted by field personnel to determine the frequency of blank collection and the analytical parameters of concern. Field blanks are created by collecting samples of laboratory supplied deionized water which have been poured into, onto or through, as appropriate, the device being decontaminated. The blank is collected after the final rinse described in Section 2.1.5 of this SSM.

2.2 Specific Procedure for Drilling and Excavation Equipment

All drilling or excavation equipment that comes in contact with the soil must be steam cleaned before use and between boreholes. This includes drill rods, bits and augers, dredges, backhoe buckets or any other large piece of equipment. Sampling devices, such as a split spoons and Shelby tubes, must be decontaminated between use, as well. An appropriate decontamination pad will be constructed to contain the solid and liquid wastes, and allow their collection for later testing and/or disposal.

2.3 Specific Procedure for Sample Pumps

Decontaminate sampling equipment prior to use in the first well and following sampling of each subsequent well. Pumps will not be removed between purging and sampling operations. The pump and tubing (including support cable and electrical wires which are in contact with the well) will be decontaminated by one of the procedures listed below.

Procedure 1

The decontaminating solutions can be pumped from either buckets or short PVC casing sections through the pump or the pump can be disassembled and flushed with the decontaminating solutions. It is recommended that detergent and isopropyl alcohol be used sparingly in the decontamination process and water flushing steps be extended to insure that any sediment trapped in the pump is removed. The pump exterior and connecting power cable must be rinsed with the decontaminating solutions as well. The procedure is as follows:

Flush the equipment/pump with potable water.

Flush with non-phosphate detergent solution. If the solution is recycled, the solution must be changed periodically.

Flush with isopropyl alcohol (reagent grade). If equipment blank data from the previous sampling event demonstrates that the level of contaminants is insignificant, then this step may be skipped.

Flush with distilled/deionized water. The final water rinse must not be recycled.

Procedure 2
Steam clean the outside of the submersible pump.

Pump hot potable water from the steam cleaner through the inside of the pump. This can be accomplished by placing the pump inside a three or four inch diameter PVC pipe with the bottom end capped. Hot water from the steam cleaner jet will be directed inside the PVC pipe and the pump exterior will be cleaned. The hot water from the steam cleaner will then be pumped from the PVC pipe through the pump and collected into another container. Note: additives or solutions should not be added to the steam cleaner.

Pump non-phosphate detergent solution through the inside of the pump. If the solution is recycled, the solution must be changed periodically.

Pump potable water through the inside pump to remove all of the detergent solution. If the solution is recycled, the solution must be changed periodically.

Pump distilled/deionized water as a final rinse through the sampling pump. The final water rinse must not be recycled.

3.0 DOCUMENTATION

Field workers shall record performance of decontamination procedures in the field logbook (see SOP-JCO-034). The following information is to be recorded at a minimum: location of decontamination: target/sampling media;

time of decontamination; list of decontaminated equipment; personnel performing decontamination; nature and identity of field blanks collected; deviations from the standard procedures; and any other relevant information. The proper documentation of decontamination procedures and blanks will be invaluable should the samples' integrity be questioned in the future.

Revision Author: _____ Date: 3-14-06
Scientist, Engineer or Technician

Reviewed: James A Bowers Date: 3/14/2006
Director, Quality Assurance Unit

K:\1-2128-2\WORKPLAN-SAP-QAPP\3-14-06DRAFT REV1\JCOSSM027.doc

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Montpelier, Vermont 05602
(802) 229-4600

Standard Operating Procedure For Use of Field Log Books

INTRODUCTION:

The use of a field log book provides an accurate and permanent record of activities, measurements and observations made in the field. A legible record of data and observations recorded in the field should be sufficient to enable others to reconstruct field events and provide sufficient evidence during legal proceedings.

PROCEDURE:

A bound notebook of waterproof paper shall be assigned to each member of the field team. A pen or an indelible marker should be used for notetaking.

Label the top of each page with the date, project name, project location, names(s) of field personnel and a page numbering sequence. The first page of each daily entry shall list the observed weather conditions; name and abbreviation of the day's personnel.

All data and observations generated during the conduct of a study, except those that are generated as direct computer input, shall be recorded directly, promptly, and legibly in ink. All data entries shall be dated on the day of entry and signed or initialed by the person entering the data. Any changes in entries shall be made so as to not obscure the original entry, shall indicate the reason for such change, and shall be dated and signed or initialed at the time of the change.

All records, which includes original field and laboratory notes and reports, shall be recorded and maintained on forms developed for the specific purpose or, in the case that such forms are not developed, in a form and manner customary to the scientific discipline.

Field notes, sketches, and data entry shall be made in indelible ink on quality paper. Surveyor's notes shall be made in a form and manner as prescribed by applicable state law and regulation and consistent with good surveying practice.

Notes and records shall be accurate, composed for orderly use, complete, clean and legible. Erasures shall not be made.

Photocopies of all fieldnotes shall be submitted to the project manager for approval and inclusion to the project files.

Revision Author: _____ Date: 3/13/96
Scientist, Engineer or Technician

Reviewed: _____ Date: 3/13/96
Director, Quality Assurance Unit

Approved: _____ Date: 3/13/96
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Standard Operating Procedure for Calibration and Operation of the Thermo Environmental Instruments Inc. Model 580B® OVM Photo-Ionization Detector

INTRODUCTION

All photo-ionization detectors (PIDs) operate on the same basic principle. A fan or pump pulls air into a chamber that is bathed in ultra-violet light. This light excites the electrons of the outer shell of the atoms of the organic molecule. The energy required to remove the outermost electrons from the molecule is called the ionization potential (IP) and is specific for any compound or atomic species (Cartier, 1989) These ions pass through a detector that measures the energy level of the gas. The more organic molecules present, the more ions, and the more energy detected. The reading is displayed on an analog meter in units of parts per million of calibration gas.

These units have individual limitations of the linear detection range and for field conditions over which they will operate. The ability to detect a chemical depends on the ability to ionize it. Therefore the IP of a chemical to be detected must be compared to the energy generated by the ultra-violet (UV) lamp of the instrument. PIDs will typically detect compounds with IPs lower than the energy of the PID lamp. The energy of lamps available are 8.3, 8.4, 9.5, 10.2, 10.6, 10.9, 11.4, 11.7, and 11.8 eV (electron volts).

EQUIPMENT LIST

A. 580B® equipped with 10.6 eV lamp
B. Zero Air gas canister
C. Span gas canister
D. Calibration hose manifold
E. Instrument logbook
F. Field book
G. Moisture trap

PROCEDURE

A. General Considerations

1. Weather: The 580B® has limited function capabilities in damp and extreme cold conditions. In these atmospheres the instrument may produce erroneous readings. Care should be taken to avoid exposure to damp atmospheres, if possible. In damp conditions the moisture trap should be inserted onto the

probe tip to prevent moisture from entering the unit. Operation of the 580B® with the moisture trap will require longer retention times to elapse before making a reading. The extra time required will depend upon a number of variables and cannot be quantified.
Extreme cold can cause the fan not to operate. Keep the 580B® in a dry, warm, secure station whenever the instrument is not in use.

Personnel Safety: The 580B® is not constructed to be intrinsically safe. The 580B® WILL ignite explosive fumes. **EXTREME CAUTION SHALL BE TAKEN TO AVOID EXPLOSIVE CONDITIONS AT ALL TIMES.** Proper testing of atmospheres with a Multi-gas Indicator (SOP-JCO-031) shall be performed prior to the use of this instrument. The 580B® will NOT be used in situations were the Multi-gas Indicator detects an ignitable atmosphere.

B. 580B® Photo-Ionization Detector Operation, Maintenance, and Calibration

The operation, maintenance and calibration of the 580B® instrument is discussed in detail in the instruction manual (Attachment JCO-036-001). This manual shall be read and reviewed prior to operating the instrument. The general guidelines for the use of the instrument are discussed below.

B.1. Instrument Check

1. While in the office, check the operational status of the 580B®.
2. Before use, make sure stainless steel filter is in place.
   a. Remove the probe from the unit
   b. Check that the stainless steel filter is in place where the probe attaches to the unit.
   c. Re-attach the probe onto the unit.
3. Replace the charger plug with the attached power plug in the "RUN/CHG" plug location.
4. Press the "ON/OFF" key to turn on the lamp and pump.
5. Hold a xylene containing marker, such as a Sharpie® in front of the detection probe. The instrument is operational if there is a visible sensor reading.
6. The 580B® may have residue contamination from previous use. Once the Sharpie® marker is drawn away from the detection probe, check the 580B® screen. The screen should return to "0.00 ppm" without fluctuations. If the display fluctuates between "0.00 ppm" and reading larger than a typical background level (say "0.04 ppm"), report the condition to the Senior Environmental Technician.

7. Calibration may not be necessary if a calibration check sequence proves accuracy of what to span gas. With the 580B® "ON" connect the regulator and tubing to the span gas cylinder. Remove the probe from the 580B® and screw on the plastic nut and tubing attached to the span gas cylinder. Turn "ON" the span gas and compare value of the span gas to the 580B® display. If response is +/- 2%, okay. Record this procedure and results in your field book along with the background reading (max 0.0 - 1.5 ppm).
8. Press the "ON/OFF" key to turn the lamp and pump off.

B.2. Calibration Procedure - To occur at "background location" on subject site (e.g., upwind, in a dry area, away from equipment operating at the site)

1. Connect regulator and tubing to the zero air gas cylinder.
2. Remove the probe from 580B® and screw on the plastic nut and tubing attached to the zero gas cylinder. DO NOT remove the stainless steel filter. (Note: DO NOT turn on the zero air valve at this time).
3. Place the chromed power plug attached to the 580B® into "RUN/CHG" port on the 580B® making certain red dot is facing upward.
4. Turn on 580B® with "ON/OFF" button ("MAX PPM" and "PPM" will appear on display)
5. Press "MODE/STORE" key:
6. Message will appear: "LOG THIS VALUE (+ = YES, - = No)" Press "-" key for No.
7. Display will show four choices: "COMM, ACCESS, PARAM, CLOCK". press "-" key to choose PARAM.
8. Message will appear: CONC METER. Press "-" key.
9. Message will appear: FREE SPACE. Press "-" key.
10. Message will appear: RESET TO CALIBRATE. Press RESET key.
11. Message will appear: RESTORE BACKUP. Press "-" key for NO (if you have to restore back-up calibration, press "+" key and continue to # 19)
12. Message will appear: "ZERO GAS RESET WHEN READY". Turn on zero air gas making sure not to block exhaust port "T" fitting or the exhaust port on the back of the 580B®. Press "RESET" key
13. Message will appear: "MODEL 580 ZEROING".
14. When the instrument has finished zeroing, a message will appear: "SPAN PPM = 100 (+ TO CONTINUE)" Do Not press "+" key yet.
15. Shut off zero air and hook up 100 ppm span gas canister to the regulator leaving the plastic nut and tubing attached to the unit. Turn on span gas and press "+" to continue.
16. Press "RESET" key when ready.
17. Message will appear: "MODEL 580 CALIBRATING" until it is through calibrating.
18. Message will appear: "RESET TO CALIBRATE" Do Not press "RESET" key. This message signifies calibration is completed.

19. At this point if any errors arise in the calibration procedure, return to Step B.2.5 in Calibration Procedure and continue.
20. Press "MODE/STORE" key to escape calibration program.
21. "MAX PPM" and "PPM" will appear on display.
22. Record the 580B® measured concentration of the span gas used (example, 100 ppm gas = 100.4 ppm), the name of the span gas, the date and user initials in the instrument log book and in the job specific fieldbook.
23. Shut off span gas. Press "ON/OFF" key to shut off 580B®, disconnect regulator and tubing from unit and canister, and reconnect probe (make sure filter is present in unit).
24. Unit is ready for use (disconnect power plug/ unit is ready to use).

B.3. Operation

1. Consult the site specific Health and Safety Plan (HASP), become familiar with its stipulations, particularly the permissible exposure limits, before performing any field work.
2. ***ALARM SETTING.*** Set the audible alarm to the action level appropriate for upgrading personal protective equipment as stated in the HASP. This is accomplished by the following:
   a. Press "MODE/STORE" key.
   b. Press "-" if message "Log this value?" appears.
   c. Screen will display "R/COMM". Choose "Parameter" mode by pressing "-".
   d. Screen will display "CONC. METER". Press "+".
   e. Screen will display "AUTO LOGGING". Press "+".
   f. Screen will display "AVERAGE =". Press "+".
   g. Screen will display "ALM AT". This is the alarm screen.
   h. The alarm setting may be changed by simultaneously holding down the "RESET" key and either the "+/INC" to change the digit above the cursor, or the "-/CRSR" switch to move the cursor.
   I. Press "MODE/STORE" to return the instrument to the "Run" mode.
3. ***MAXIMUM CONCENTRATION HOLD.***
   a. Press "MODE/STORE" key.
   b. Press "-" if message "Log this value?" appears.
   c. Screen will display "R/COMM". Choose "Parameter" mode by pressing "-".
   d. Screen will display two lines of text. Top line reads "Conc.Meter". When bottom line of text reads "Reset To CHG", press "Reset" to change the "Run" mode.
   e. Screen will now display "Max Hold", "+ = USE/ - = NO"
   f. Press "+" to select the "Max Hold" option.

g. The 580B® 580B must be operated in the "Max Hold" mode. The screen will display both the current detection as well as the maximum concentration detected during operation.

4. ***BATTERY INDICATOR.*** While in the "Run" mode, a flashing "B" in the left hand corner indicates that the battery is low. The battery should be recharged at this time.
5. ***FIELD WORK.*** Enter the work area from the "background location", frequently viewing the display to monitor breathing space readings.
6. Conduct the tasks required according to the appropriate protocol, frequently observing breathing space readings and recording them in the job specific fieldbook, along with the time and location of the reading.
7. Confirm that the instrument held its calibration by connecting the span gas canister to the 580B® as described in Section B.2 and noting the concentration reading. Note this calibration confirmation in the instrument log book and in the job specific fieldbook.
8. After use turn the instrument off and reconnect the instrument to the battery charger (there is no danger of overcharging).

C. Records

1. Records shall be kept of the use and calibration of the instrument and maintained in a permanent file.
2. Any anomalies or equipment damages should be immediately reported, via written report memorandum, to the Senior Environmental Technician.

D. Decontamination

1. Wipe the outside of the instrument case, display, straps and cables that are attached to the instrument with a cloth dampened with distilled or deionized water. Dry the instrument immediately with a dry clean cloth.

2. **CARE SHALL BE TAKEN TO KEEP WATER FROM ENTERING THE TIP ASSEMBLY OF THE INSTRUMENT.**

REFERENCE

Cartier and Associates, 1989, General Safety and Health Provisions, OSHA 1910.120, Accompanying looseleaf course text, pp IX-14.

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Site Specific Method for Low Stress Groundwater Sampling of Monitoring Wells and Piezometers

INTRODUCTION

A primary goal of a groundwater sampling program is to accurately assess the quality of the groundwater that occurs under the study site. To accomplish this goal, specific measures must be taken during groundwater sampling to ensure that the sample from each well is representative of the aquifer water in that locality. Measures must also be taken so that the samples are not altered or contaminated during the sampling and handling procedures. Low Stress sampling methods are generally more effective than bailer sampling techniques at accomplishing this goal.

For the purposes of this discussion, there are three zones of water in a well, the stagnant water in the casing, the water in the screened interval, and the formation water drawn into the well by purging. Stagnant water is unlikely to be representative of groundwater quality and should not be included in the sample. The concept of Low Stress sampling is to pump out the water in the screened interval, draw in the formation water, and leave the stagnant casing water undisturbed and in place. Purging is continued until indicator parameters measured in the purge water are stable (usually less than 2 well volumes). Dedicated tubing or pumps are the preferred.

Some data from previous sampling events are necessary in order to successfully perform Low Stress Groundwater Sampling of Monitoring Wells. At a minimum these data include:

- A description of the reference measuring point (usually the top of casing)
- The depth from the measuring point to the sampling point (usually the center of the screen)

Other required data are listed in Form JCO-HYDRO-010 (Attachment SSM-JCO-053-2).

When practical, the wells should be sampled in order of increasing probable chemical concentrations. The least contaminated well should be sampled first, and the most contaminated last.

Any field deviations from this method must be documented and technically justified in accordance with SOP-JCO-018 Standard Operating Procedure for Deviation from Protocols or Standard Operating Procedures and for Notation, Correction, and Documentation of Unforseen Circumstances.

PROCEDURE

Prior to commencing, the well should be unlocked, and a plastic sheet laid on the ground around the well. The field forms and chain of custody records should be prepared, and the type of equipment being used recorded.

A. Water Level Measurement

Prior to collecting the water level reading, if organic contamination is suspected to be present, a photoionization detector measurement of the headspace of the well should be recorded immediately upon opening the well cap. This measurement should be made with a calibrated photoionization detector at the rim of the well. Calibration and use of photoionization detectors is described in SOP-JCO-032 and SOP-JCO-041.
A water level measurement shall be taken prior to well purging (refer to SOP-JCO-009 for procedure).

Extreme care should be taken to avoid disturbing the water column in the well. No attempt should be made to measure the total depth of the well until AFTER sampling is completed. If water levels are measured automatically with a transducer and data-logger (or other method), manual measurements are still necessary prior to and after purging and sampling.

B. Well Purging

The sampling and purging equipment should be lowered gently and smoothly to avoid stirring up particulates. If possible, the pump or tubing intake should be placed at the center of the screened interval and at least three feet below the static water level, or at predetermined project and well specific depths. Do not move the pump or intake position after purging has commenced until the sampling is complete. The intake should be located at the same depth for each successive sampling event. For open-hole bedrock wells the sampling equipment should be located at the center of primary flow zones. The end of the sampling equipment should be at least two feet above the bottom of the well in order to avoid disturbing silt in the well sump.

There should not be extra coils of tubing at the surface. The tubing should have as large a diameter as practical, taking into account the well recharge rate, well diameter, etc. Generally tubing inside diameter should be less than 3/8 to 1/2 inch in order to insure a continuous water column in the tubing.

There are a variety of sample withdrawal mechanisms that can be used to collect water samples. The type of system used is a function of the degree of detail the study requires, well construction, the water level, the type of pollutant, the analytical procedure and the presence or absence of permanent pumping fixtures within the well (Scalf, et al, 1981). Ideally, the sample mechanism should be completely inert to the analytes of interest. However, materials such as polyethylene, which can sorb contaminants, may be acceptable if the equipment is dedicated to a single well.

If a gasoline or diesel generator or compressor is used, it should be located a minimum of 30 feet downwind from the well head in order to prevent cross contamination by airborne exhaust constituents.

The tubing should remain full of water during purging and sampling to avoid changes to the water chemistry by contact with the atmosphere. If the tubing does not remain full, a narrower tube may be inserted within the original tube. Other possible actions are constriction of the tubing with a clamp, or reducing the pumping rate.

Bailers are not suitable for sampling with low stress sampling techniques. Positive displacement ("WaTerra" type) check valve pumps are also generally not suitable for sampling with low stress sampling techniques.

Acceptable low stress sampling equipment includes: down-hole electric pumps, bladder pumps, and peristaltic pumps. Each has its own advantages and disadvantages.

1. Down-hole submersible electric pumps. When feasible, down-hole electric pumps should be dedicated to each well, as lowering the pump into the well will disturb the static water column. Grundfos and other high volume down-hole submersible electric pumps are satisfactory in large diameter wells and in aquifers with high hydraulic conductivity. For most monitoring wells they typically cannot maintain the low flow rates required for slow purging. Low volume downhole electric pumps may be satisfactory if the components are of suitable materials. One type of low volume pump is the Whale pump, which can be operated with a 12 volt DC power source, and can pump at rates less than 1 gallon per minute.

2. Bladder pumps. When feasible, bladder pumps should be dedicated to each well, as lowering the pump into the well will disturb the static water column. Bladder pumps supply water in pulses, which can make it difficult to determine when equilibrium is reached. For aquifers where the depth to groundwater is greater than 20 feet, bladder pumps often provide the best available technology for low stress sampling. The bladder pump discharge rate for is commonly 0.5 gallons per minute.

   One type of bladder pump is manufactured by Q.E.D. and is typically equipped with Teflon bladders. A portable compressor and control box connected at the well head to the air line of the sampling pump provide the mechanism for well water evacuation. The pump operates by compressed air squeezing the bladder in the pump casing, thereby forcing the column of water in the Teflon water line up and out of the well.

   The effectiveness of the bladder pump is based on the proper placement of the pump within the well. If the bladder is not entirely submerged within the water column, the possibility of air entering the sampling train is distinct. Therefore, when installing the pumps, care must be taken to insure that the bladder is entirely submerged. All material construction in the sampling train is either Teflon or stainless steel, thereby providing an inert environment for the well water sample.

3. Peristaltic pumps. In many cases Peristaltic pumps provide the least expensive and most versatile option for low stress sampling. Peristaltic pumps may cause loss of volatile organic compounds due to the vacuum used to draw the water to the ground surface, although the significance of the loss is disputed among experts (Puls and Barcelona, 1995). Peristaltic pumps are limited to locations where the groundwater level is within about 20 feet of the ground surface. The deeper the groundwater, the more volatilization of contaminants during purging/sampling. Volatilization is reduced by placing in-line sample bottle holders on the suction side of the pump.

   One type of peristaltic pump is made by Geotech. This pump has a variable controller to adjust the rate of flow. It is powered by a 12 volt DC battery such as a deep cell marine battery.

Purge Rate - The purge rate should be kept consistent during each sampling event and between sampling events. The purge rate should be far less than the rate of pumping used to initially develop the well and should be such that the water level in the well is maintained within 10 cm (~0.3 feet) of the normal water level measured prior to purging. If the initial purge rate draws down the water level more than 0.3 feet, the rate should be reduced. If the static water level is above the screened interval, care should be taken to avoid drawing the water level down below the top of the screened interval. Note that for low-yield bedrock wells with long water columns above the intake point, it may not be possible to sample at a low enough rate to prevent on-going drawdown during the purging. In this event, the purge rate should be decreased to as low as is feasible, and the water column monitored until the rate of drawdown is constant over three measurements.

Under no circumstances should the well be pumped dry. If the well is pumped dry by some unforeseen circumstances, the sampler should leave the sampling equipment in the well, proceed with other wells, and return to the well later for sample collection. The sample should then be collected directly from the first water drawn from the well without waiting for parameter stabilization. If the well is still dry after some time (e.g. 2 hours minimum), it should be left overnight if at all possible; otherwise, a note should be made stating why the sample was not collected. In low permeability aquitards, where the recharge rate is so slow that the well cannot be purged without pumping it dry, it is better to sample (from the screened interval with dedicated equipment) without purging, rather than pumping it dry.

Purged well water should be collected in a graduated cylinder (after passing through the flow cell) in order to quantify the volume of water that is evacuated. Purge time, water level, and purge rate/volume should be recorded every 3-5 minutes. Longer recording times are acceptable if purge time exceeds 30 minutes and purge rates are unaltered. The volume of water to purge is determined by the stabilization of field measured indicator parameters during purging.

Indicator Parameters - Field measured indicator parameters should be measured and recorded every 3-5 minutes with a flow through cell during purging, and include at a minimum: Dissolved oxygen, Specific Conductance, Temperature, pH, turbidity, and ORP. Longer periods for measurement are acceptable if the purge time exceeds 30 minutes without stabilization. The sample port or in-line sample bottle holders should be BEFORE the flow through cell, and the peristaltic pump, if one is used, should be AFTER the flow through cell. *Care should be taken to avoid placing a vacuum on the flow cell that is greater than the maximum specified for the probes.* If necessary, the flow cell may be placed on the downstream side of the pump to prevent rupture of the probe sensors.
Stabilization is defined as three consecutive readings collected at 3-5 minute intervals which are within the following limits:

- pH ± 0.1 unit
- Temperature ± 0.2 degrees C
- Specific Conductance ± 3%
- ORP ± 10 mvolts
- dissolved oxygen ± 0.3 mg/L
- turbidity ± 10% for values between 1 and 100 NTU or less than 1 NTU.

A minimum of five measurements shall be collected prior to sampling. If conditions do not stabilize within two hours of purging, document that information on the field sheet, and report the median of the last five measurements for those parameters which did not stabilize.

Final water oxidation-reduction potential (ORP) results for groundwater shall be reported as field results and Standard Hydrogen Electrode adjusted (equations and constants used shall also be reported).

Flow cells should be clear (except for turbidity measurements), and designed to be kept full of water (without bubbles) during operation. They should not allow water to return to the well when the pump is turned off. They should not leak air, and the probes should be completely submerged. One such flow-cell system is a YSI 3560™ Water Quality Monitoring System. This system allows for chemical parameters to be monitored during the well purging process, within the flow cell.

If indicator parameters have not stabilized after two hours of purging, proceed with sample collection as described below. Record all data and attempts to achieve stabilization, and include a comment on the chain of custody reflecting the fact that stabilization was not achieved.

C. Sample Collection

The sample is collected after the well has been purged. The same equipment used for purging should be used for sampling. Sampling may be accomplished by two methods, from an in-line sample port or from an in-line sample bottle holder. The in-line bottle holder method is preferred, as the sample does not come in contact with air, thereby preventing possible volatilization of contaminants. Sampling should be accomplished from an in-line sample port or sample bottle holder up-stream of the flow cell and peristaltic pump (if one is used). The rate of pumping during sampling should be the same as that used for purging. If in-line sample bottle holders are used, the pump should be shut off and the bottles should be removed one at a time. Additional water can be collected in the bottle cap if necessary to

completely fill the bottles. If an in-line sample port is used sample containers should be filled by allowing the pump discharge to flow down the side of the container with minimum turbulence. VOC samples should be collected first.

D. Sample Size and Preservation

Parameter-specific requirements are given for preservation, sample size, holding time, and analytical methodology in Attachment SSM-JCO-053-1. Alternative requirements may be necessary for specific projects.

1. Major Ions For major ionic species, two 1-liter plastic bottles are used: a pale yellow primary (with HNO_3 preservative) for metals and; a secondary for the other inorganics (no preservative). Collect the sample by removing the cap carefully from the sample bottle, taking care not to touch the inside of the cap or bottle with the sampling spigot. The sample container is filled to approximately one-inch below the top of the one-liter plastic bottle, and the bottle is capped tightly.

2. Volatile Organic Compounds (VOC) Samples shall be collected in 40 mL glass vials with screw-on caps equipped with Teflon lined septa. Ordinarily clear glass is adequate, but if the parameters of concern are typified by a high photolysis potential, brown glass should be utilized. The sample vial should be filled slowly and carefully. Care must be taken to minimize turbulence. The vial shall be filled to a positive meniscus and the cap screwed on firmly. The vial should be inverted and tapped gently with a finger to check for air bubbles. There should be no bubbles in the sample vial immediately after sample collection. In some cases bubbles may form in the vial over time as the sample degasses. Vials should be stored in the cooler with the cap downward to prevent loss if bubbles form.

3. Dissolved Metals Generally filtering dissolved metals samples is not necessary or desirable. If filtering is required (if you are comparing filtered and un-filtered samples for instance) it should be done in the field, not in the laboratory. If filtering is used, do not acidify samples until AFTER they are filtered.

4. Pesticides The pesticide samples should be collected in clean 1 liter amber glass bottles with Teflon lined septa. The sample is collected by removing the cap carefully from the sample bottle, taking care not to touch the inside of the cap or bottle with the sampling spigot or any other apparatus. For some pesticides, a pre-rinse with isopropyl alcohol is recommended. The sample bottle is partially filled and rinsed with the well water. The sample bottle is then filled entirely, taking care not to introduce air bubbles. The bottle is tightly capped and sealed with tape.

E. Documentation of Sample

Documentation of the sampling event will consist of logging data on Form SOP-JCO-HYDRO-010, the Groundwater Sampling Data Form. This form is presented in Attachment SSM-JCO-053-2.

F. Transportation/Packing

Upon collection, a sample label is fixed to each bottle. The label will include data written in permanent ink. The label data will include the site name, the well name, the date and time, the type of analysis, the preservative, and the sampler's initials. The sample is then packed in an insulated cooler with ice or cold packs and delivered to the laboratory for analysis as soon as is reasonable, but shipped no later than 24 hours after collection. A completed Chain-of-Custody Form (SOP-JCO-007) will accompany the sample set.

References

Scalf, M.R., McNabb, J.F., Dunlap, W.J., Cosby, R.L., and J.F. Fryberger, 1981. Manual of Ground Water Sampling Procedures, National Water Well Assn., Worthington, OH, 1982.

Puls, R.W. And Barcelona, M.J., 1995, Low-Flow (Minimal Drawdown) Ground-water Sample Procedures, EPA Ground Water Issue EPA/540/S-95/504

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Attachment SSM-JCO-053-1

Sample Parameters, Methods, Volumes, Containers, Preservation and Holding Times

(following pages)

From "Field Methods Manual". State of Vermont Dept. of Environmental Conservation

6.4 SAMPLE PRESERVATION AND HOLD TIMES

Measurement	Container	Preservative	Maximum Hold Time
PHYSICAL			
Color	P, G	Cool, 4° C	48 hours
Conductance	P, G	Cool, 4° C	28 days, if filtered
Percent Solids	P, G	Cool, 4° C	ASAP
Residue			
Filterable	P, G	Cool, 4° C	7 days
Non-Filterable	P, G	Cool, 4° C	7 days
Total	P, G	Cool, 4° C	7 days
Volatile	P, G	Cool, 4° C	7 days
Temperature	P, G	None required	Analyze Immediately
Turbidity	P, G	Cool, 4° C	48 hours
CHEMICAL			
Alkalinity	P, G	Cool, 4° C	14 days
BOD	P, G	Cool, 4° C	48 hours
COD	P, G	pH <2 (2ml H_2SO_4/L) Cool, 4° C	28 days
Chlorophyll	P, G	Dark, cool, 4° C	6 hours
Chlorine	P	None	Analyze Immediately
Cyanide	P, G	pH >12 (2ml 10 N NaOH/L) and 0.06 g ascorbic acid/L Cool, 4° C	24 hours
Hardness	P, G	pH <2 (2ml HNO_3/L) Cool, 4° C	6 months
Oil & Grease	G only	pH <2 (5 ml 1:1 HCl/L) Cool, 4° C	28 days

6.4 (Continued)

Measurement	Container	Preservative	Maximum Hold Time
Oxygen Dissolved			
Probe	G only	None required	Analyze Immediately
Winkler	G only	Store in dark $MnSO_4$, I-/Azide	8 hours
Phenolics	G only	$CuSO_4$, H_3PO_4 Cool, 4^oC	24 hours
pH	P, G	Cool, 4^o C	ASAP
NUTRIENTS			
Chloride	P, G	None required	28 days
Nitrogen			
Ammonia	P, G	pH <2 (2 ml H_2SO_4/L) Cool, 4^o C	28 days
Kjeldahl, Total	P, G	pH <2 (2 ml H_2SO_4/L) Cool, 4^o C	28 days
Nitrate/ Nitrite	P, G	pH <2 (2 ml H_2SO_4/L) Cool, 4^o C	28 days
Nitrate	P, G	Cool, 4^o C	48 hours
Nitrite	P, G	Cool, 4^o C	48 hours
Phosphorus, Total	G	None required	28 days
Ortho Phosphorus	G	Cool, 4^o C	48 hours
Sulfate	P, G	Cool, 4^o C	28 days
METALS			
Total, Dissolved	P, G	pH <2 (2 ml HNO_3/L) Cool, 4^o C	6 months
Chromium, Hex.	P, G	Cool, 4^o C	24 hours

6.4 (Continued)

Measurement	Container	Preservative	Maximum Hold Time
Mercury	P,G	pH <2 (2 ml HNO_3/L)	28 days
BACTERIOLOGICAL			
Fecal coliform	P only	Cool, 4° C	.6 hours
Total coliform	P only	Cool, 4° C	6 hours
Fecal strep	P only	Cool, 4° C	6 hours
ORGANICS	If chlorinated: $Na_2S_2O_3$:		
Method 801	G vial	Cool, 4° C	14 days
Method 802	G vial	Cool, 4° C pH <2 w 1:1 HCl	14 days
Method 824	G vial	Cool, 4° C	14 days
Propane	G vial	Cool, 4° C	14 days
Method 827	G Amber	Cool, 4° C	7 days to extraction 40 days after
Method 808	G Amber	Cool, 4° C	7 days to extraction 40 days after

NOTE: G = Glass
P = Plastic (Nalgene)

ENDYNE, INC.

Laboratory Services

32 James Brown Drive
Williston, Vermont 05495
(802) 879-4333
FAX 879-7103

SAMPLING AND PRESERVATION OF SAMPLES

PARAMETER	METHOD	VOLUME REQUIRED mls	CONTAINER*	PRES.	HOLD. TIME days
Acid/Base/ Neutral	625	2/1000	G/T	4 C	7/40
IAP		2000	P	4 C	
-pH	150.1				immediate
-Cl	325.3				28
-NH_3	350.3	plus			28
-NO_2	354.1				2
-NO_3	353.3				2
-TKN	351.4				28
-TP	365.2	250	G		28
-TDP	365.2	250	G		28
-BOD_5	405.1				2
-Alkalinity	310.1				14
Residual Chlorine	330.5	100	G/T	none	immediate
COD	410.1	100	P,G/T	H_2SO_4 pH<2	28
Color	110.2	100	P,G/T	4 C	2
Conductance	120.1	100	P,G/T	4 C	28
Cyanides	600.	1000	P,G/T	NaOH pH>12	14
Fluoride	340.2	100	P	none	28
Foaming Agent MBAS	425.1	400	P,G/T	4 C	2
Metals, Diss.	200series	1000	P	filter,HNO_3	180
Metals,Total	200series	1000	P	digest,HNO_3	180
Oil + Grease	413.1	2/1000	G/T	HCl pH<2	14
Total Hydrocarbons	418.1	2/1000	G/T	HCl pH<2	14

SAMPLING AND PRESERVATION OF SAMPLES

PARAMETER	METHOD	VOLUME REQUIRED mls	CONTAINER*	PRES.	HOLD. TIME days
Pesticides + PCB's	608	2/1000	G/T	4 C	7/40
Phenols		500	G/T	H_2SO_4 pH<2	14
Purgeables	8240,8010 8020,624 601,602	2/40	G/T	4 C no bubbles	14
Purgeables	502.2	2/40	G	Na_2SO_4 4 C	14
Solids, Settleable	160.5	1000	P,G/T	4 C	2
Solids, Total	160.3	100	P,G/T	4 C	7
TSS	160.2	100	P,G/T	4 C	7
TDS	160.1	100	P,G/T	4 C	7
TVS	160.4	100	P,G/T	4 C	7
Sulfide		500	P,G/T	2 ml ZnAc	7
Sulfite		100	P,G/T	none	immediate
TOC		500	G/T	H_2SO_4 pH<2	28
Total Coliform		125	P(sterile)	4 C	6 hours
Fecal Coliform		125	P(sterile)	4 C	6 hours
Turbidity	180.1	100	P,G/T	4 C	2
Herbicides	509B	2/1000	G	4 C	14

* P = Plastic
  G = Glass
  T = Teflon Seal

of [illegible] ibution, 1200 South Eads Street, Arlington VA 22202. Cost: $9.25 (subject to change). Table IA.

(13) "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," by M.J. Fishman and Linda C. Friedman; U.S. Geological Survey Open File Report 85-495 (1986). Available from U.S. Geological Survey, Western Distribution Branch, Box 24525, Denver Federal Center, Denver, CO 80225. Cost $108.75 (subject to change). Table IB, Note 1.

(14) "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," N.W. Skougstad and others, editors; USGS TWRI, Book 5, Chapter A1 (1979). Available from U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Cost $10.00 (subject to change). Table IB, Note 7.

(15) "Methods for Analysis of Organic Substances in Water," by D.F. Goerlitz and Eugene Brown; USGS TWRI, Book 5, Chapter A3 (1972). Available from U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Cost $0.90 (subject to change). Table IB, Note 23; Table ID, Note 4.

(16) "Water Temperature—Influential Factors, Field Measurement and Data Presentation," by H.H. Stevens, Jr., J. Ficke, and G.F. Smoot; USGS TWRI Book 1, Chapter D1, 1975. Available from U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Cost $1.60 (subject to change). Table IB, Note 31.

(17) "Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters," by M.J. Fishman and Eugene Brown; U.S. Geological Survey Open File Report 76-77 (1076). Available from U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Cost $13.50 (subject to change). Table IE, Note 2.

(18) Official Methods of Analysis of the Association of Official Analytical Chemicals, methods manual, 14th Edition (1985). Price: $145.50. Available from: The Association of Official Analytical Chemicals, 1111 N. 19th Street, Suite 210, Arlington, VA 22209. Table IB, Note 2.

(19) "American National Standard on Photographic Processing Effluents," April 2, 1975. Available from: American National Standards Institute, 1430 Broadway, New York, New York 10018. Table IB, Note 8.

(20) "An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color," NCASI Technical Bulletin No. 253, December 1971. Available from: National Council of the Paper Industry for Air and Stream Improvements, Inc., [illegible]SWE, dated February 10, 1976, Technicon AutoAnalyzer II, Method and pr[illegible] able from Technicon Industrial [illegible] Tarrytown, New York 10591, Table [illegible], Note 6.

(22) Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis 1979, Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537. Table IB, Note 13.

(23) OIC Chemical Oxygen Demand Method, Method and price available from Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, Texas 77840. Table IB, Note 12.

(24) ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977, Method and price available from Orion Research Incorporation, 840 Memorial Drive, Cambridge, Massachusetts 02138. Table IB, Note 15.

(25) Bicinchoninate Method for Copper, Method 8506, Hach Handbook of Water Analysis, 1979, Method and price available from Hach Chemical Company, P.O. Box 300, Loveland, Colorado 80537. Table IB, Note 18.

(26) Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon AutoAnalyzer II, Method and price available from Technicon Industrial Systems, Tarrytown, New York 10591. Table IB, Note 20.

(27) 1, 10-Phenanthroline Method for Iron, Hach Method 8000, Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537. Table IB, Note 21.

(28) Periodate Oxidation Method for Manganese, Method 8034, Hach Handbook for Water Analysis, 1979, Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537. Table IB, Note 22.

(29) Nitrite Nitrogen, Hach Method 8507, Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537. Table IB, Note 24.

(30) Zincon Method for Zinc, Method 8009, Hach Handbook for Water Analysis, 1979, Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537. Table IB, Note 32.

(31) "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," by R.F. Addison and R.G. Ackman, Journal of Chromatography, Volume 47, No. 3, pp. 421-426, 1970. Available in most public libraries. Back volumes of the Journal of Chromatography are available from Elsevier/North-Holland, Inc., Journal Information Centre, 52 Vanderbilt Avenue, New

tor in the Region or State where the discharge will occur may determine for a particular discharge that additional parameters or pollutants must be reported. Under such circumstances, additional test procedures for analysis of pollutants may be specified by the Regional Administrator, or the Director upon the recommendation of the Director of the Environmental Monitoring and Support Laboratory, Cincinnati.

(d) Under certain circumstances, the Administrator may approve, upon recommendation by the Director, Environmental Monitoring and Support Laboratory, Cincinnati, additional alternate test procedures for nationwide use.

(e) Sample preservation procedures, container materials, and maximum allowable holding times for parameters cited in Tables IA, IB, IC, ID, and IE are prescribed in Table II. Any person from a specific discharge. Applications for variances may be made by letters to the Regional Administrator in the Region in which the discharge will occur. Sufficient data should be provided to assure such variance does not adversely affect the integrity of the sample. Such data will be forwarded by the Regional Administrator to the Director of the Environmental Monitoring and Support Laboratory in Cincinnati, Ohio for technical review and recommendations for action on the variance application. Upon receipt of the recommendations from the Director of the Environmental Monitoring and Support Laboratory, the Regional Administrator may grant a variance applicable to the specific discharge to the applicant. A decision to approve or deny a variance will be made within 90 days of receipt of the application by the Regional Administrator.

TABLE II—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter No./name	Container[1]	Preservation[2,3]	Maximum holding time[4]
Table IA—Bacterial Tests			
1-4. Coliform, fecal and total	P, G	Cool, 4°C, 0.008% $Na_2S_2O_3$[5]	6 hours
5. Fecal streptococci	P, G	do	Do
Table IB—Inorganic Tests			
1. Acidity	P, G	Cool, 4°C	14 days
2. Alkalinity	P, G	do	Do
4. Ammonia	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days.
9. Biochemical oxygen demand	P, G	Cool, 4°C	48 hours
11. Bromide	P, G	None required	28 days
14. Biochemical oxygen demand carbonaceous	P, G	Cool, 4°C	48 hours
15. Chemical oxygen demand	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days.
16. Chloride	P, G	None required	Do
17. Chlorine, total residual	P, G	do	Analyze immediately
21. Color	P, G	Cool, 4°C	48 hours
23-24. Cyanide, total and [illegible]amenable to chlorination	P, G	Cool, 4°C, NaOH to pH > 12, 0.6g ascorbic acid	14 days[6]
25. Fluoride	P	None required	28 days
27. Hardness	P, G	HNO_3 to pH < 2, H_2SO_4 to pH < 2	6 months
28. Hydrogen [illegible]	[illegible]	None required	Analyze immediately
31, 43. Kjeldahl [illegible]	[illegible]	Cool, 4°C, H_2SO_4 to pH < 2	28 days
Metals:[7]			
18. Chromium [illegible]	[illegible]	[illegible], 4°C	24 hours
35. Mercury	P, G	HNO_3 to pH < 2	28 days
3, 5-8, 10, 12, [illegible] 34, 36, [illegible] 70-72, 74, 75. Metals except chromium VI and mercury	P, G	[illegible]	6 months
38. Nitrate	P, G	Cool, 4°C	48 hours.
39. Nitrate-nitrite	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days
40. Nitrite	P, G	Cool, 4°C	48 hours.
41. Oil and grease	G	Cool, 4°C, H_2SO_4 to pH < 2	28 days

30-142 O[illegible]

Parameter No./name	Container [1]	Preservation [2,3]	Maximum hol
42 Organic carbon	P, G	Cool, 4°C, HCl or H_2SO_4 to pH < 2	Do.
44 Orthophosphate	P, G	Filter immediately, Cool, 4°C	48 hours.
46 Oxygen, Dissolved Probe	G Bottle and top.	None required	Analyze immediately.
47 Winkler	do	Fix on site and store in dark	8 hours.
48 Phenols	G only	Cool, 4°C, H_2SO_4 to pH < 2	28 days.
49 Phosphorus (elemental)	G	Cool, 4°C	48 hours.
50 Phosphorus, total	P, G	Cool, 4°C, H_2SO_4 to pH < 2	28 days.
53. Residue, total	P, G	Cool, 4°C	7 days.
54. Residue, Filterable	P, G	do	7 days.
55 Residue, Nonfilterable (TSS)	P, G	do	7 days
56 Residue, Settleable	P, G	do	48 hours.
57 Residue, volatile	P, G	do	7 days.
61 Silica	P	do	28 days.
64 Specific conductance	P, G	do	Do.
65 Sulfate	P, G	do	Do.
66 Sulfide	P, G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH > 9.	7 days.
67 Sulfite	P, G	None required	Analyze immediately.
68 Surfactants	P, G	Cool, 4°C	48 hours
69 Temperature	P, G	None required	Analyze
73 Turbidity	P, G	Cool, 4°C	48 hours
Table IC—Organic Tests [4]			
13 18-20, 22, 24-28, 34-37, 39-43, 45-47, 56 66, 88, 89, 92-95, 97 Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$ [5]	14 days
6, 57, 90 Purgeable aromatic hydrocarbons	do	Cool, 4°C, 0.008% $Na_2S_2O_3$, HCl to pH2 [6]	Do.
3, 4, Acrolein and acrylonitrile	do	Cool, 4°C, 0.008% $Na_2S_2O_3$; Adjust pH to 4-5 [7,8]	Do
23, 30, 44, 49, 53, 67, 70, 71, 83, 85, 96 Phenols [11]	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$ [5]	7 days until extraction, 40 days after extraction.
7, 38 Benzidines [11]	do	do	7 days until extraction.[9]
14, 17, 48, 50-52 Phthalate esters [11]	do	Cool, 4°C	7 days until extraction; 40 days after extraction.
72-74 Nitrosamines [11,12]	do	Cool, 4°C, store in dark, 0.008% $Na_2S_2O_3$ [5]	Do.
76-82 PCBs [11] acrylonitrile	do	Cool, 4°C	Do.
54, 55 65, 69 Nitroaromatics and isophorone [11]	do	Cool, 4°C, 0.008% $Na_2S_2O_3$ [5] store in dark.	Do.
1, 2, 5, 8-12, 32, 33, 58, 59, 64, 68, 84, 86, Polynuclear aromatic hydrocarbons. [11]	do	do	Do.
15, 16, 21, 31, 75 Haloethers [11]	do	Cool, 4°C, 0.008% $Na_2S_2O_3$ [5]	Do.
29, 35-37, 60-63, 91 Chlorinated hydrocarbons [11]	do	Cool, 4°C	Do
87 TCDD [11]	do	Cool, 4°C, 0.008% $Na_2S_2O_3$ [5]	Do.
Table ID—Pesticides Tests:			
1-70 Pesticides [11]	do	Cool, 4°C, pH 5-9 [13]	Do
Table IE—Radiological Tests			
1-5 Alpha, beta and radium	P, G	HNO_3 to pH < 2	6 months

Table II Notes

[1] Polyethylene (P) or Glass (G)

[2] Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

[3] When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater), and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

[4] Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or

time if knowledge exists to show that this is necessary to maintain sample stability. See § 136.3(e) for details.

[5] Should only be used in the presence of residual chlorine.

[6] Maximum holding time is 24 hours when sulfide is present. Optionally all samples m[illegible]ested with lead acetate p[illegible] before pH adjustments in order to determine if sulfide is present. If sulfide is present, it [illegible]an be removed by the additio[illegible] cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH [illegible]

[7] Samples should be filtered immediately on-site before adding preservative for dissolved metals.

[8] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

[9] Sample receiving no pH adjustment must be analyzed within seven days of sampling.

[10] The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment m[illegible] be analyzed within 3 days of sampling.

[11] When the extractable analytes of concern fall within a single chemical category, the specified preservative and maxi[illegible] holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within tw[illegible] more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% so[illegible] thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven [illegible] before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure [illegible] noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analys[illegible] benzidine).

[12] If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangemer[illegible] benzidine.

[13] Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosp[illegible]

[14] For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hour[illegible] sampling.

[15] The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the sample is extra[illegible] within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$.

[38 FR 28758, Oct. 16, 1973, as amended at 41 FR 52781, Dec. 1, 1976; 49 FR 43251, 432[illegible] 43259, Oct. 26, 1984; 50 FR 691, 692, 695, Jan. 4, 1985; 51 FR 23693, June 30, 1986; 52 [illegible] 33543, Sept. 3, 1987]

EDITORIAL NOTE: Information collection requirements contained in § 136.3(e) have been approved by the Office of Management and Budget and are not effective, pend[illegible] OMB approval.

§ 136.4 Application for alternate test procedures.

(a) Any person may apply to the Regional Administrator in the Region where the discharge occurs for approval of an alternative test procedure.

(b) When the discharge for which an alternative test procedure is proposed occurs within a State having a permit program approved pursuant to section 402 of the Act, the applicant shall submit his application to the Regional Administrator through the Director of the State agency having responsibility for issuance of NPDES permits within such State.

(c) Unless and until printed application forms are made available, an application for an alternate test procedure may be made by letter in triplicate. Any application for an alternate test procedure under this paragraph (c) shall:

(1) Provide the name and address of the responsible person or firm making the discharge (if not the applicant) and the applicable ID number of the existing or pending permit, issuing agency, and type of permit for which the alternate test procedure is requested, and the discharge serial number.

(2) Identify the pollutant or parar[illegible]ter for which approval of an altern[illegible] testing procedure is being requested.

(3) Provide justification for usi[illegible] testing procedures other than th[illegible] specified in Table I.

(4) Provide a detailed description [illegible] the proposed alternate test procedu[illegible] together with references to publish[illegible] studies of the applicability of the [illegible]ternate test procedure to the effluc[illegible] in question.

(d) An application for approval of [illegible] alternate test procedure for nati[illegible] wide use may be made by letter in t[illegible] licate to the Director, Environmer[illegible] Monitoring and Support Laborat[illegible] Cincinnati, Ohio 45268. Any appli[illegible] tion for an alternate test proced[illegible] under this paragraph (d) shall:

(1) Provide the name and addres[illegible] the responsible person or firm mak[illegible] the application.

(2) Identify the pollutant(s) [illegible] parameter(s) for which nationwi[illegible]e proval of an alternate testing pr[illegible] dure is being requested.

(3) Provide a detailed description [illegible] the proposed alternate procedure, [illegible] gether with references to publishe[illegible] other studies confirming the gen[illegible] applicability of the alternate test [illegible] cedure to the pollutant(s)

Attachment SSM-JCO-053-2

Groundwater Sampling Data Form

(Form JCO-HYDRO-010, 11/96)

THE JOHNSON COMPANY, INC.
100 State Street, Suite 600
Montpelier, Vermont 05602

FORM-JCO-HYDRO-010 (Rev. 1/97)

JCO File No.:_____

SLOW PURGE GROUNDWATER SAMPLING DATA FORM

Date:_____ Project Name:_____ Project #:__-_____-____ Site/Well No._____

Location:_____Time On-site: _____

Coded/Replicate No._____ Sampler:_____ Weather:_____ COC #:_____

WELL DATA

Description of Measuring Point (MP):_____

[1]MP Height Above/Below Ground Surface:_____ft [1]MP Elevation:_____ [1]Original Total Pipe Length :_____ ft

Outside Casing Diameter :_____in Casing Material :_____ [1]Screen Material :_____

[1]Screen Center Depth BMP:_____ft [1]Screen Length :_____ft [1]Outside Screen Diameter :_____in

[1]Sand Pack Diameter :_____in [1]Sand Pack Top/Bottom Depth BMP :_____/_____ft [1]Total Drill Depth BGS :_____ft

[1]Initial Development Rate:_____gpm or mL/min [1]Previous Event Final Purge Rate:_____ gpm or mL/min

[1]Previous Event Volume Purged:_____ gal or mL [1]Previous Event Pump/Setting :_____

[1]Previous Event Tubing Used --- Length:___feet I.D:_____in or cm Material:_____

Initial Water Depth Below MP:_____ft Pump/Setting This Event:_____

Tubing Used This Event (if not dedicated) --- Length:_____feet I.D:_____in or cm Material:_____

Volume of Sampling Equipment:_____gal or mL Depth to Intake BMP this Sampling Event:_____ft

Purge Water Disposal:_____ Decontamination Method:_____

SAMPLING DATA/FIELD PARAMETERS

Color:_____ Odor:_____ Appearance:_____

Sample Name and/or Number	Parameter	Container	Preservative	Time	Volume Purged
				:_____	
				:_____	
				:_____	
				:_____	
				:_____	
				:_____	
				:_____	
				:_____	
				:_____	

Remarks:_____

Final Depth to Water Below MP:_____feet Total Well Depth Below MP: _____feet Time Off-Site:_____

Initial/Final Volume of Water in Well: _____/_____mL or gal.

Well volumes in- Gal./ft for various outside casing diameters. 0.50" = 0.01 0.75" = 0.023 1.0" = 0.041 1.25" = 0.064
1.50" = 0.09 2.00" = 0.16 2.50" = 0.25 3.00" = 0.32 3.50" = 0.50 4.00" = 0.65 6.00" = 1.47

[1]Data to be transcibed from previous sampling event form or well installation log if available and applicable

THE JOHNSON COMPANY, INC.
100 State Street, Suite 600
Montpelier, Vermont 05602

FORM-JCO-HYDRO-010 (Rev. 1/97)

JCO File No.:_____

Date:_____ Project Name: _____ Project #:____-_____-____ Site:_____ Sampler:_____

PURGE DATA FIELD PARAMETERS

Sample Name and/or Number	**Sample Depth** *(ft BMP or BGS)*	**Equip+ Inject. Vol.** *(mL)*	**Time** *(hr:min:sec)*	**Elapsed Purge/Drive Time** *Units* (_____)	**Purge Vol.** *Units* (_____)	**Purge Rate** *Units* (_____)	**Depth to Water** *(ft BMP)*	**DO** *(mg/kg)*	**Specific Cond.** *(µmho/cm)*	**Temp.** *(°C/°F)*	**pH** *(Std. units)*	**Turbid.** *(NTU)*	**ORP** *(mV)*	**Other** _____ *Units* (_____)

Use Additional Pages as Necessary

THE JOHNSON COMPANY, INC.
100 State Street, Suite 600
Montpelier, Vermont 05602
(802) 229-4600

SITE SPECIFIC METHOD FOR CALIBRATION AND USE OF THE YSI MODEL 610XL, THE DRT-15CE AND LAMOTTE 2020 TURBIDIMETERS, AND THE HACH DR890 COLORIMETER FOR FERROUS IRON ANALYSIS

The YSI 610 XL, the turbidimeters, and the HACH colorimeter are used for monitoring field parameters during sampling of seeps, surface water, and Low Stress Groundwater Sampling (as discussed in Environmental Protection Agency Standard Operating Procedure (SOP) GW-0001 ("*Low Stress Purging and Sampling Procedure*").

The YSI 610 XL is a multi-parameter data sonde used to track field parameters in groundwater. The YSI 600 XL (Sonde) is specified with the following sensors: pH; Temperature; Specific Conductance; Oxidation-Reduction (Redox) Potential; and Dissolved Oxygen.

The HF Scientific DRT-15CE and Lamotte 2020 turbidimeters are used with manufacturer supplied bottles to measure the turbidity of grab samples.

The HACH DR890 colorimeter is used with manufacturer supplied reagents sealed in vacuum bottles to measure the concentration of ferrous iron in aqueous samples.

Instrument calibrations will be executed in accordance with:

- http://pubs.water.usgs.gov/twri9A. [Chapter updates and revisions are ongoing and are summarized at http://water.usgs.gov/owq/FieldManual/mastererrata.html]
- Manufacturer recommendations
- EPA Region I DRAFT 1998 Guidelines (attached)

The Standard Hydrogen Electrode conversion will be done for final ORP measurements in accordance with the manufacturer's documentation, with constants and equations documented in the report.

YSI CALIBRATION PROCEDURE:

The most common method of supplying power to the Sonde is through the YSI 610 Display/Logger module which is rechargeable, and when connected, powers the Sonde off its internal battery. If the display module is not used with the Sonde, i.e., if a laptop computer is used to display the Sonde readings, then the Sonde must be powered off an external supply. This method addresses use of the YSI with the Display/Logger unit. In the event another form of use is required, i.e., direct connection to a laptop computer, then the user is referred to the YSI Operations Manual. A fully charged display module should provide between 6-8 hours of field operation, so it is important that the display module be fully recharged after each day's use.

Equipment Check List:

[ ] YSI 610 XL
[ ] YSI 600 Display/Logger Module
[ ] YSI Flow Cell Attachment
[ ] Calibration kit which contains: pH standard buffer solutions, conductivity standards, barometer or altimeter (for barometric pressure), a zero dissolved oxygen standard, Zobell Redox standard solutions, and a thermometer traceable to National Institute for Standards and Technology (NIST).
[ ] Connecting cable

Calibration:
Calibrate according to U.S. EPA Region 1 Draft Calibration of Field Instruments (attached). The temperature should be calibrated first, and the thermister replaced if the reading is incorrect by more than 0.2 degrees C. All calibration fluids should be brought to the same temperature. Two standards shall be used for pH, conductivity, and Redox. The probes are fixed together in a flow-through cell, and they will be rinsed three times with distilled water, and three times with the standard fluid, prior to calibrating with each fluid. Calibration shall be considered acceptable if the instrument derived value for the second standard is within 5% of the published value for that standard and: 0.1 standard unit for pH, and less than 0.2 mg/L dissolved oxygen for the zero standard.

Sampling:
1. The Sonde is ready for deployment at the well head following connection to the Display module and Flow Cell. Once the Sonde is connected to the display module, it will automatically display readings in the "run" mode of the module.

2. All field parameters during groundwater sampling will be collected pursuant to the EPA Region I SOP-GW-0001 ("*Low Stress Purging and Sampling Procedure*"). The Sonde must be connected to a flow through cell such that the field parameters are monitored while the monitoring well is slowly purged prior to sampling.

QA/QC:
1. The YSI will be calibrated on a daily basis, due to the atmospheric fluctuations for the DO meter. The calibration shall be checked against the standards at the end of each day of use, and the results recorded in the instrument specific calibration field sheet or field book.

TURBIDIMETER CALIBRATION PROCEDURE:

Equipment Check List:
[ ] Turbidimeter
[ ] 1 and 10 NTU standards

Calibration:
Calibrate according to the manufacturers instructions (attached). Calibration shall be considered acceptable if the instrument derived value for the second standard is within 5% of the published value for that standard.

Sampling:
1. Fill the manufacturer supplied vial with the liquid to be tested. Insert the vial in the meter, and orient it as directed in the manufacturers instructions. If applicable, close the lid and record the digital readout of the turbidity.

2. Empty and clean the vial immediately after measurement. Rinse the vial a minimum of three times with distilled water. If the liquid being tested has high dissolved solids, it may be necessary to rinse the vial with dilute hydrochloric acid, followed by a distilled water rinse, to dissolve precipitates on the glass walls of the vial.

QA/QC:
1. The turbidimeter will be calibrated on a daily basis. The calibration shall be checked against the standards at the end of each day of use, and the results recorded in the instrument specific calibration field sheet or field book.

HACH DR890 FERROUS IRON CALIBRATION AND MEASUREMENT PROCEDURE:

Equipment Check List:
[ ] Hach DR890 colorimeter
[ ] Ferrous Iron Ampules
[ ] Manufacturer Supplied Sample Cells
[ ] 1000 ug/L concentration Ferrous Iron Standard

Calibration:
Check calibration by measuring standard solution according to the manufacturers instructions (attached). Calibration shall be considered acceptable if the instrument derived value for the second standard is within 10% of the published value for that standard. If calibration is not acceptable then prepare five diluted standards at concentrations between 10 and 1000 ug/L, and calibrate according to the manufacturers instructions (attached)

Sampling:
1. Fill the manufacturer supplied sample cell vial with at least 10 mL of the liquid to be tested (the blank). Insert the blank vial in the meter, orient it as directed in the manufacturers instructions, and cover it tightly with the cap. Press ZERO.

2. Fill a ferrous Iron AccuVac Ampul with sample by inverting the Ampule into the sample and breaking the stem of the Ampul. Invert the ampul several times to mix. Wipe off liquid and fingerprints. Press TIMER ENTER to start a three-minute stop watch for the reaction. After three minutes, place the ampule into the cell holder and cover it tightly. Press READ and the ferrous iron concentration will be displayed in mg/L.

QA/QC:
2. The colorimeter calibration will be checked (and calibrated if necessary) on a daily basis. The calibration shall be checked against the standard at the end of each day of use, and the results recorded in the instrument specific calibration field sheet or field book.

REFERENCES:
1. U.S. EPA Region 1, 1998. Draft Calibration of Field Instruments, June 3, 1998.
2. Operations Manual for YSI 600 XL
3. EPA SOP-GW-0001 ("*Low Stress Purging and Sampling Procedure*").

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Reviewed: _____ Date: 3/14/2006
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Attachment SSM-JCO-055-1

US EPA Region 1 June 3, 1998 Draft Calibration of Field Instruments

(following 12 pages)

SAS

U.S. ENVIRONMENTAL PROTECTION AGENCY
REGION 1

DRAFT CALIBRATION OF FIELD INSTRUMENTS
(temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction potential [ORP], and turbidity)

I. SCOPE & APPLICATION

The purpose of this standard operating procedure (SOP) is to provide a framework for calibrating field instruments used to measure water quality parameters for ground water and surface water. Water quality parameters include temperature, pH, dissolved oxygen, conductivity/specific conductance, oxidation/reduction potential [ORP], and turbidity. This SOP supplements, but does not replace, EPA analytical methods listed in 40 CFR 136 and 40 CFR 141 for temperature, dissolved oxygen, conductivity/specific conductance, pH and turbidity.

This SOP is written for instruments that utilize multiple probes (temperature, pH, dissolved oxygen, conductivity/specific conductance, and/or oxidation/reduction potential [ORP]) and the probe readings for pH, dissolved oxygen, and specific conductance are automatically corrected for temperature. Communications to the instrument (programming and displaying the measurement values) are performed using a display/logger or a computer. Information sent to the instrument is entered through the keypad on the display/logger or computer. It is desirable that the display/logger or computer have data storage capabilities. If the instrument does not have a keypad, follow the manufacturer's instructions for entering information into the instrument.

For ground water monitoring, the instrument must be equipped with a flow-through-cell, and the display/logger or computer display screen needs to be large enough to simultaneously contain the readouts of each probe in the instrument. Turbidity is measured using a separate instrument because turbidity cannot be measured in a flow-through-cell. This procedure is applicable for use with the EPA Region 1 Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells.

II. GENERAL

All monitoring instruments must be calibrated before they are used to measure environmental samples. Part of the calibration is performed prior to the field event. For instrument probes that rely on the temperature sensor (pH, dissolved oxygen, conductivity/specific conductance, and

oxidation/reduction potential [ORP]), each temperature sensor needs to be checked for accuracy against a thermometer that is traceable to the National Institute of Standards and Technology (NIST). Before any instrument is calibrated or used to perform environmental measurements, the instrument must stabilize (warm-up) according to manufacturer's instructions.

Most instruments will require at least two standards to bracket the expected measurement range, that is, one standard less than the expected value and one higher. Calibration must be performed at the beginning of each sampling day prior to sample collection. To determine if the instruments have remained in calibration during transport to each sampling location, use one of the previously used standards as a check standard at the sampling site. If the check measurement does not agree with the initial calibration or to within the specifications of the instrument, then the instrument must be re-calibrated. When an environmental sample measurement falls outside the calibration range, the instrument must be re-calibrated to bracket the new range before continuing measurements.

This SOP requires that the manufacturer's instruction manual (including the instrument specifications) accompany the instrument into the field.

III. CALIBRATION PROCEDURES

Prior to calibration, all instrument probes must be cleaned according to the manufacturer's instructions. Failure to perform this step (proper maintenance) can lead to erratic measurements.

Program the multi-probe instrument so that the following parameters to be measured will be displayed: temperature, pH, percent dissolved oxygen, mg/l dissolved oxygen, conductivity, specific conductance, and ORP.

The volume of the calibration solutions must be sufficient to cover both the probe and temperature sensor (see manufacturer's instructions for additional information).

While calibrating or measuring, make sure there are no air bubbles lodged between the probe and the probe guard.

TEMPERATURE

Most instrument manuals state there is no calibration of the temperature sensor, but the temperature sensor must be checked to determine its accuracy. This accuracy check is performed

at least once per year and the accuracy check date/information is kept with the instrument. If the accuracy check date/information is not included with the instrument or the last check was over a year, the temperature sensor accuracy needs to be checked at the beginning of the sampling event. If the instrument contains multiple temperature sensors, each sensor must be checked.

Verification Procedure

1. Allow a container filled with water to come to room temperature.

2. Place a thermometer that is traceable to the National Institute of Standards and Technology (NIST), and the instrument's temperature sensor into the water and wait for both temperature readings to stabilize.

3. Compare the two measurements. The instrument's temperature sensor must agree with the reference thermometer measurement within the accuracy of the sensor (usually ±0.15°C). If the measurements do not agree, the instrument may not be working properly and the manufacturer needs to be consulted.

pH (electrometric)

The pH of a sample is determined electrometrically using a glass electrode.

Choose the appropriate buffered standards that will bracket the expected values at the sampling locations. For ground water, the pH will usually be close to seven. Three standards are needed for the calibration: one close to seven, one at least two pH units below seven and the other at least two pH units above seven. For those instruments that will not accept three standards, the instrument will need to be re-calibrated if the water sample's pH is outside the initial calibration range described by the two standards.

Calibration Procedure

1. Allow the buffered standards to equilibrate to the ambient temperature.

2. Fill calibration containers with the buffered standards so each standard will cover the pH probe and temperature sensor.

3. Remove probe from its storage container, rinse with distilled water, blot dry with soft tissue.

4. Select monitoring/run mode. Immerse probe into the initial standard (e.g., pH 7).

5. Stir the standard until the readings stabilize. If the reading does not change within 30 seconds, select calibration mode and then select "pH". Enter the buffered standard value into instrument. Select monitoring/run mode. The readings should remain within manufacturer's specifications; if they change, re-calibrate. If readings continue to change after re-calibration, consult manufacturer.

6. Remove probe from the initial standard, rinse with distilled water, and blot dry.

7. Immerse probe into the second standard (e.g., pH 4). Repeat step 5.

8. Remove probe from the second standard, rinse with distilled water, and blot dry. If instrument only accepts two standards, the calibration is complete. Go to step 11. Otherwise continue.

9. Immerse probe in third buffered standard (e.g., pH 9) and repeat step 5.

10. Remove probe from the third standard, rinse with distilled water, and blot dry.

11. Select monitoring/run mode, if not already selected. To ensure that the initial calibration standard (e.g., pH 7) has not changed, immerse the probe into the initial standard. Wait for the readings to stabilize. The reading should read the initial standard value within the manufacturer's specifications. If not, re-calibrate the instrument. If re-calibration does not help, the calibration range may be too great. Reduce calibration range by using standards that are closer together.

12. The calibration is complete. Place pH probe in its storage container.

DISSOLVED OXYGEN

Dissolved oxygen (DO) content in water is measured using a membrane electrode. The DO probe's membrane and electrolyte solution should be replaced prior to the sampling period. Failure to perform this step may lead to erratic measurements.

Calibration Procedure

1. Gently dry the temperature sensor according to manufacturer's instructions.

2. Place a wet sponge or a wet paper towel on the bottom of the DO calibration container.

3. Place the DO probe into the container without the probe coming in contact with the wet sponge or paper towel. The probe must fit tightly into the container to prevent the escape of moisture evaporating from the sponge or towel.

4. Allow the confined air to become saturated with water vapor (saturation occurs in approximately 10 to 15 minutes). During this time, turn-on the instrument to allow the DO probe to warm-up. Select monitoring/run mode. Check temperature readings. Readings must stabilize before continuing to the next step.

5. Select calibration mode; then select "DO %".

6. Enter the local barometric pressure (usually in mm of mercury) for the sampling location into the instrument. This measurement must be determined from an on-site barometer. Do not use barometric pressure obtained from the local weather services unless the pressure is corrected for the elevation of the sampling location. [Note: inches of mercury times 25.4 mm/inch equals mm of mercury or consult Oxygen Solubility at Indicated Pressure chart attached to the SOP for conversion at selected pressures].

7. The instrument should indicate that the calibration is in progress. The instrument will take approximately one minute to calibrate. After calibration, the instrument should display percent saturated DO.

8. Select monitoring/run mode. Compare the DO mg/l reading to the Oxygen Solubility at Indicated Pressure chart attached to the SOP. The numbers should agree. If they do not agree to the accuracy of the instrument (usually ± 0.2 mg/L), repeat calibration. If this does not work, change the membrane and electrolyte solution.

9 Remove the probe from the container and place it into a 0.0 mg/L DO standard (see note). The standard must be filled to the top of its container and the DO probe must fit tightly into the standard's container (no head space). Check temperature readings. They must stabilize before continuing.

10. Wait until the "mg/l DO" readings have stabilized. The instrument should read 0.0 mg/L or to the accuracy of the instrument (usually ± 0.2 mg/L). If the instrument cannot reach these values, it will be necessary to clean the probe, and change the membrane and electrolyte solution. If this does not work, prepare a new 0.0 mg/L DO standard. If these measures do not work, contact manufacturer.

Note: To prepare a zero mg/L DO standard follow the procedure stated in Standard Methods (Method 4500-O G). The method basically states to add excess sodium sulfite (until no more dissolves) and a trace amount of cobalt chloride to water. The standard container must be completely filled (no head space). This solution is prepared prior to the sampling event. If some of the solution is lost during instrument calibration, add more water to the container so that the standard is stored with no head space.

SPECIFIC CONDUCTANCE

Conductivity is used to measure the ability of an aqueous solution to carry an electrical current. Specific conductance is the conductivity value corrected to 25°C.

Most instruments are calibrated against a single standard which is near, but below the specific conductance of the environmental samples. A second standard which is above the environmental sample specific conductance is used to check the linearity of the instrument in the range of measurements.

Calibration Procedure:

1. Allow the calibration standard to equilibrate to the ambient temperature.

2. Remove probe from its storage container, rinse the probe with a small amount of the conductivity/specific conductance standard (discard the rinsate), and place the probe into the conductivity/specific conductance standard.

3. Select monitoring/run mode. Wait until the probe temperature has stabilized.

4. Look up the conductivity value at this temperature from the conductivity versus temperature correction table usually found on the standard bottle or on the standard instruction sheet. You may need to interpolate the conductivity value between temperatures. Select calibration mode, then conductivity. Enter the temperature corrected conductivity value into the instrument.

5. Select monitoring/run mode. The reading should remain within manufacturer's specifications. If it does not, re-calibrate. If readings continue to change after re-calibration, consult manufacturer.

6. Read the specific conductance on the instrument and compare the value to the specific conductance value on the standard. The instrument value should agree with the standard within the manufacturer's specifications. If not, re-calibrate. If the re-calibration does not correct the problem, the probe may need to be cleaned or serviced by the instrument manufacturer.

7. Remove probe from the standard, rinse the probe with a small amount of the second conductivity/specific conductance standard (discard the rinsate), and place the probe into the second conductivity/specific conductance standard. The second standard will serve to verify the linearity of the instrument. Read the specific conductance value from the instrument and compare the value to the specific conductance on the standard. The two values should agree within the specifications of the instrument. If they do not agree, re-calibrate. If readings do not compare, then the second standard may be outside the linear range of the instrument. Use a standard that is closer, but above the first standard and repeat the verification. If values still do not compare, try cleaning the probe or consult the manufacturer.

8. When monitoring ground water or surface water, use the specific conductance readings.

OXIDATION/REDUCTION POTENTIAL (ORP)

The oxidation/reduction potential is the electrometric difference measured in a solution between an inert indicator electrode and a suitable reference electrode. The electrometric difference is measured in millivolts and is temperature dependent.

Calibration or Verification Procedure

1. Allow the calibration standard (a Zobell solution) to equilibrate to ambient temperature.

2. Remove the probe from its storage container, and place it into the standard.

3. Select monitoring/run mode.

4. While stirring the standard, wait for the probe temperature to stabilize, then read the temperature.

5. Look up the millivolt (mv) value at this temperature from the millivolt versus temperature correction table usually found on the standard bottle or on the standard instruction sheet. You may need to interpolate millivolt value between temperatures. Select "calibration mode", then "ORP". Enter the temperature-corrected ORP value into the instrument.

6. Select monitoring/run mode. The readings should remain unchanged within manufacturer's specifications. If they change, re-calibrate. If readings continue to change after re-calibration, consult manufacturer.

7. If the instrument instruction manual states that the instrument is factory calibrated, then verify the factory calibration against the standard. If they do not agree within the specifications of the instrument, the instrument will need to be re-calibrated by the manufacturer.

TURBIDITY

The turbidity method is based upon a comparison of intensity of light scattered by a sample under defined conditions with the intensity of light scattered by a standard reference suspension. A turbidimeter is a nephelometer with a visible light source for illuminating the sample and one or more photo-electric detectors placed ninety degrees to the path of the light source.

Some instruments will only accept one standard. For these instruments, the standards will serve as check points.

Calibration Procedures

1. Allow the calibration standards to equilibrate at the ambient temperature. The use of commercially available polymer primary standards (AMCO-AEPA-1) is preferred, however, the standards can be prepared using Formazin according to the EPA analytical Method 180.1.

2. If the standard cuvette is not sealed, rinse a cuvette with deionized water. Shake the cuvette to remove as much water as possible. Do not wipe dry the inside of the cuvette because lint from the wipe may remain in the cuvette. Add the standard to the cuvette.

3. Before performing the calibration procedure, make sure the cuvettes are not scratched and the outside surfaces are dry, free from fingerprints and dust. If the cuvette is scratched or dirty, discard or clean the cuvette respectively.

4. Zero the instrument by using either a zero or 0.02 NTU standard. A zero standard (approximately 0 NTU) can be prepared by passing distilled water through a 0.45 micron pore size membrane filter.

5. Using a standard in the range of 0 - 20 NTUs, calibrate according to manufacturer's instructions or verify calibration if instrument will not accept a second standard. If verifying, the instrument should read standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used during the sampling event with a standard that falls within that range.

6. Using a standard between 20 and 100 NTUs, calibrate according to manufacturer's instructions or verify calibration if instrument does not accept a third standard. If verifying, the instrument should read standard value to within the specifications of the instrument. If the instrument has range of scales, check each range that will be used with the proper standard for that scale.

IV. DATA MANAGEMENT AND RECORDS MANAGEMENT

All calibration records must be documented in the project's log book. At a minimum, include the instrument manufacturer, model number, instrument identification number, standards used to calibrate the instruments (including source), calibration date, and the instrument readings.

References

Standard Methods for the Examination of Water and Wastewater, 19th edition, 1995.

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

Turbidity - Methods for the Determination of Inorganic Substances in Environmental Samples, EPA/600/R-93/100, August 1993.

Oxygen Solubility at Indicated Pressure

Temp.	Pressure (Hg)							
	760	755	750	745	740	735	730	mm
°C	29.92	29.72	29.53	29.33	29.13	28.94	28.74	in
0	14.57	14.47	14.38	14.28	14.18	14.09	13.99	mg/l
1	14.17	14.08	13.98	13.89	13.79	13.70	13.61	
2	13.79	13.70	13.61	13.52	13.42	13.33	13.24	
3	13.43	13.34	13.25	13.16	13.07	12-98	12.90	
4	13.08	12.99	12.91	12.82	12.73	12.65	12.56	
5	12.74	12.66	12.57	12.49	12.40	12.32	12.23	
6	12.42	12.34	12.26	12.17	12.09	12.01	[illegible]	
7	12.11	12.03	11.95	11.87	11.79	11.71	[illegible]	
8	11.81	11.73	11.65	11.57	11.50	11.42	11.34	
9	11.53	11.45	11.38	11.30	11.22	[illegible]	11.07	
10	11.28	11.19	11.11	11.04	10.96	[illegible]	10.81	
11	10.99	10.92	10.84	10.77	10.70	[illegible]	[illegible]	
12	10.74	10.67	10.60	10.53	10.45	[illegible]	[illegible]	
13	10.50	10.43	10.36	10.29	10.22	10.15	[illegible]	
14	10.27	10.20	10.13	10.06	10.00	9.93	[illegible]	
15	10.05	9.98	9.92	9.85	9.78	[illegible]	9.65	
16	9.83	9.76	9.70	9.63	9.57	[illegible]	9.43	
17	9.63	9.57	9.50	9.44	[illegible]	[illegible]	9.24	
18	9.43	9.37	9.30	9.24	[illegible]	[illegible]	[illegible]	
19	9.24	9.18	9.12	9.05	[illegible]	[illegible]	[illegible]	
20	9.06	9.00	8.94	8.88	8.82	[illegible]	[illegible]	
21	8.88	8.82	8.76	[illegible]	8.64	8.58	[illegible]	
22	8.71	8.65	8.59	[illegible]	8.47	8.42	8.36	
23	8.55	8.49	8.43	[illegible]	[illegible]	8.26	8.20	
24	8.39	8.33	[illegible]	8.22	[illegible]	[illegible]	8.05	
25	8.24	8.18	[illegible]	8.07	[illegible]	[illegible]	7.90	
26	8.09	8.03	[illegible]	7.92	[illegible]	7.81	7.76	
27	7.95	7.90	[illegible]	7.79	[illegible]	7.68	7.62	
28	7.81	7.76	[illegible]	7.65	7.60	7.54	7.49	
29	7.68	7.63	[illegible]	7.52	7.47	7.42	7.36	
30	[illegible]	[illegible]	7.43	[illegible]	7.34	7.29	7.24	
31	[illegible]	[illegible]	7.32	[illegible]	7.22	7.16	7.11	
32	[illegible]	[illegible]	7.20	7.15	7.10	7.05	7.00	
33	7.08	[illegible]	7.08	7.03	6.98	6.93	6.88	
34	7.07	7.02	6.97	6.92	6.87	6.82	6.78	
35	6.95	6.90	6.85	6.80	6.76	6.71	6.66	
36	6.84	6.79	6.76	6.70	6.65	6.60	6.55	
37	6.73	6.68	6.64	6.59	6.54	6.49	6.45	
38	6.63	6.58	6.54	6.49	6.44	6.40	6.35	
39	6.52	6.47	6.43	6.38	6.35	6.29	6.24	
40	6.42	6.37	6.33	6.28	6.24	6.19	6.15	
41	6.32	6.27	6.23	6.18	6.14	6.09	6.05	
42	6.22	6.18	6.13	6.09	6.04	6.00	5.95	
43	6.13	6.09	6.04	6.00	5.95	5.91	5.87	
44	6.03	5.99	5.94	5.90	5.86	5.81	5.77	
45	5.94	5.90	5.85	5.81	5.77	5.72	5.68	

(Continued)

Source: Draft EPA Handbook of Methods for Acid Deposition Studies. Field Operations for Surface Water Chemistry. EPA/600/4-89/020. August 1989.

Oxygen Solubility at Indicated Pressure (continued)

Temp.	Pressure (Hg)								
	725	720	715	710	705	700	695	690	mm
°C	28.54	28.35	28.15	27.95	27.76	27.56	27.36	27.17	in
0	13.89	13.80	13.70	13.61	13.51	13.41	13.32	13.22	mg/l
1	13.51	13.42	13.33	13.23	13.14	13.04	12.95	12.86	
2	13.15	13.06	12.07	12.88	12.79	12.69	12.60	12.51	
3	12.81	12.72	12.63	12.54	12.45	12.36	12.27	12.18	
4	12.47	12.39	12.30	12.21	12.13	12.04	11.95	11.87	
5	12.15	12.06	11.98	11.89	11.81	11.73	11.64	11.56	
6	11.84	11.73	11.68	11.60	11.51	11.43	11.35	11.2	
7	11.55	11.47	11.39	11.31	11.22	11.14	11.06	10.9	
8	11.26	11.18	11.10	11.02	10.95	10.87	10.79	10.7	
9	10.99	10.92	10.84	10.76	10.69	10.61	10.53	10.4	
10	10.74	10.66	10.59	10.51	10.44	10.36	10.29	10.21	
11	10.48	10.40	10.33	10.28	10.18	10.11	10.04	9.96	
12	10.24	10.17	10.10	10.02	9.95	9.88	9.81	9.46	
13	10.01	9.94	9.87	9.80	9.73	9.66	9.59	9.52	
14	9.79	9.72	9.65	9.68	9.51	9.45	9.38	9.31	
15	9.58	9.51	9.44	9.58	9.31	9.24	9.18	9.11	
16	9.37	9.30	9.24	9.17	9.11	9.04	8.97	8.91	
17	9.18	9.11	9.05	8.98	8.92	8.86	8.79	8.73	
18	8.99	8.92	8.86	8.80	8.73	8.67	8.61	8.54	
19	8.81	8.74	8.68	8.62	8.56	8.45	8.43	8.3	
20	8.63	8.57	8.51	8.45	8.39	8.34	8.27	8.21	
21	8.46	8.40	8.34	8.28	8.22	8.16	8.10	8.04	
22	8.30	8.24	8.18	8.12	8.06	8.00	7.95	7.89	
23	8.15	8.09	8.03	7.97	7.91	7.86	7.80	7.74	
24	7.99	7.94	7.88	7.82	7.76	7.71	7.65	7.59	
25	7.85	7.79	7.73	7.68	7.60	7.55	7.51	7.46	
26	7.70	7.65	7.59	7.54	7.48	7.43	7.37	7.32	
27	7.57	7.52	7.46	7.41	7.35	7.30	7.25	7.19	
28	7.44	7.38	7.33	7.28	7.22	7.17	7.12	7.06	
29	7.31	7.26	7.21	7.15	7.10	7.05	7.00	6.94	
30	7.19	7.14	7.08	7.03	6.98	6.93	6.88	6.82	
31	7.06	7.01	6.96	6.91	6.86	6.81	6.76	6.70	
32	6.95	6.90	6.85	6.80	6.70	6.70	6.64	6.59	
33	6.83	6.78	6.73	6.68	6.83	6.58	6.53	6.48	
34	6.73	6.68	6.63	6.58	6.53	6.48	6.43	6.38	
35	6.61	6.56	6.51	6.47	6.42	6.37	6.36	6.27	
36	6.51	6.46	6.41	6.36	6.31	6.27	6.22	6.17	
37	6.40	6.35	6.31	6.26	6.21	6.16	6.12	6.07	
38	6.30	6.26	6.21	6.16	6.12	6.07	6.02	5.98	
39	6.26	6.15	6.11	6.06	6.01	5.97	5.92	5.87	
40	6.10	6.06	6.01	5.96	5.92	5.86	5.83	5.78	
41	6.01	5.96	5.91	5.87	5.82	5.78	5.73	5.69	
42	5.91	5.86	5.82	5.77	5.73	5.69	5.64	5.60	
43	5.82	5.78	5.73	5.69	5.65	5.60	5.56	5.51	
44	5.72	5.68	5.64	5.59	5.55	5.51	5.46	5.42	
45	5.64	5.59	5.55	5.51	5.47	5.42	5.38	5.34	

Source: Draft EPA Handbook of Methods for Acid Deposition Studies, Field Operations for Surface Water Chemistry. EPA/600/4-89/020. August 1989.

THE JOHNSON COMPANY, INC.
100 State Street, Suite 600
Montpelier, Vermont 05602
(802) 229-4600

Attachment SSM-JCO-055-2

Lamotte and HF Scientific Turbidimeter Calibration Instructions

(following 8 pages)

LaMotte

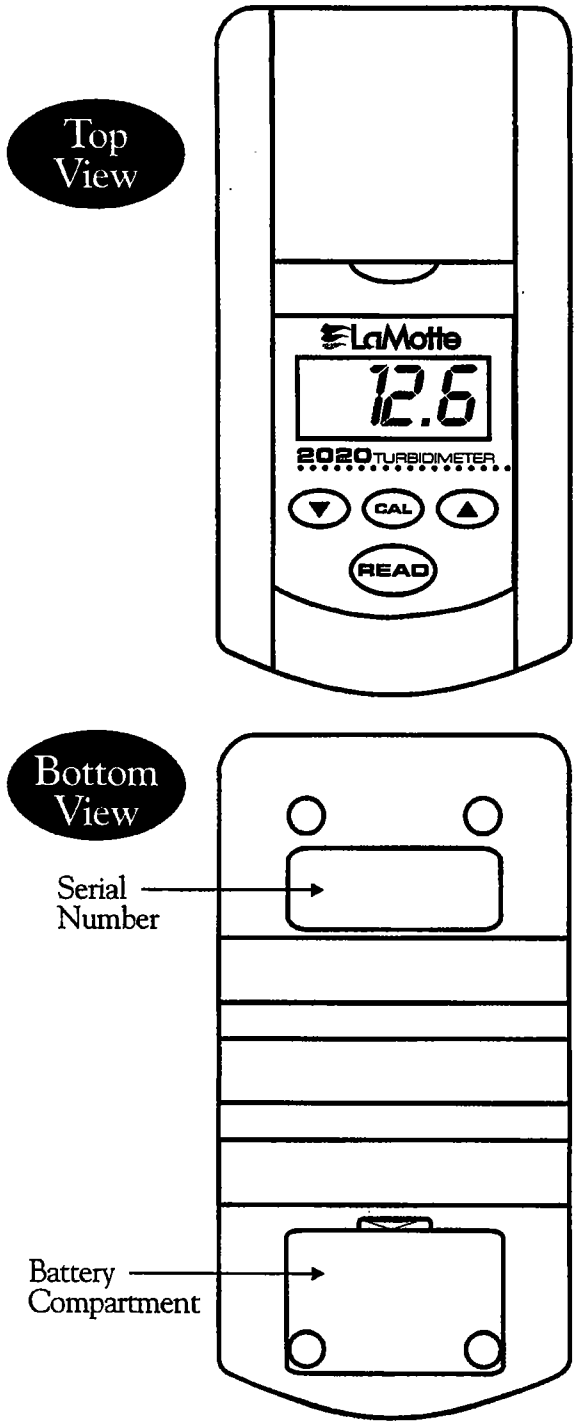
Johnson Co / 802-229-4600

2020 TURBIDIMETER

JCO-2

Instruction MANUAL

* clean vials w/ HCl !

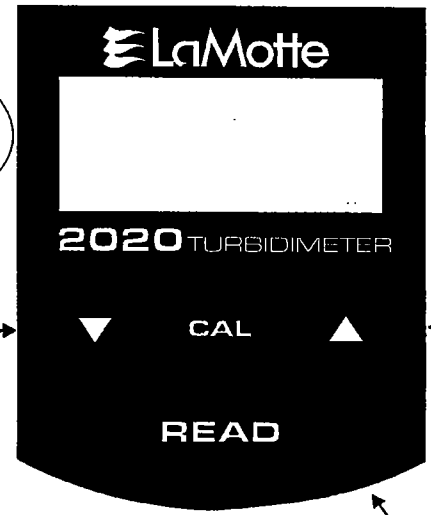


THE KEYPAD

The DISPLAY will display turbidity reading with the following resolution:
0.00 - 10.99 NTU; 11.0 - 109.9 NTU; 110 - 1100 NTU

- When the **READ** button is first pushed, a number will be briefly displayed that indicates the software version number.
- A walking dash "-" will be displayed when measurement is taking place.
- The display will flash after the **CAL** button has been pushed during the calibration procedure until the **CAL** button has been pushed again to enter the adjusted value.
- "OFF" will be displayed after the **READ** button has been held down for 1 second. The meter will turn off when the button is released.
- "Er1" will be displayed when the battery voltage is very low.
- "Er2" will be displayed when measured turbidity is over range (1100 NTU).
- "Er3" will be displayed when the bulb has burned out or the tube is misaligned.
- "BAT" will be displayed when the battery voltage is getting low. Readings are reliable. Replace battery as soon as possible.
- "▲" will be displayed when the meter is in EPA mode.

See TROUBLE SHOOTING GUIDE page 23



The DOWN ARROW will **DECREASE** the numerical value of the display while in calibration mode.

The UP ARROW will **INCREASE** the numerical value of the display while in calibration mode.

The READ button is used to turn the meter ON and to take readings. Pressing the button for 1 second will cause the meter to display OFF. Releasing the button when OFF is displayed turns the meter OFF.

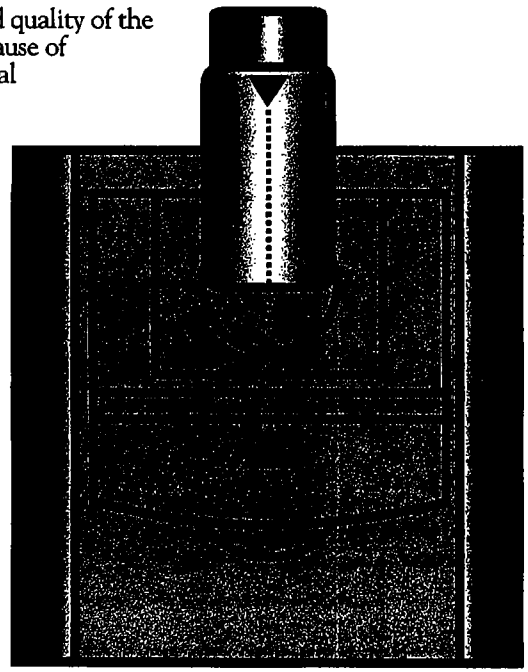
The CAL button is used for **CALIBRATION** procedures and to change between standard operating mode and EPA mode.

TURBIDITY TUBES

Turbidity tubes should always be washed prior to use. Use a mild detergent to remove any dirt or finger prints. Dry the outside of the turbidity tubes with a clean, lint-free cloth or disposable wipe. Allow the turbidity tubes to air-dry in an inverted position to prevent dust from entering the tube.

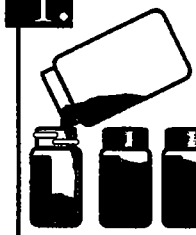
The handling of the turbidity tubes is of utmost importance. Scratches, fingerprints and water droplets on the turbidity tube or inside the light chamber can cause stray light interference leading to inaccurate results. It is imperative that the turbidity tubes and light chamber be clean and dry. Scratches and abrasions will permanently affect the accuracy of the readings. The inside of the tubes can be acid washed periodically and coated with special silicon oil to mask imperfections in the glass. Avoid acid contact with the black ink on the outside of the tubes. After a tube has been filled and capped, it should be held by the cap and the outside surface should be wiped with a clean, lint-free absorbent cloth until it is dry and smudge-free. Handling the tube only by the cap will avoid problems from fingerprints. Always set the clean tube aside on a clean surface that will not contaminate the tube.

Variability in the geometry and quality of the glassware is the predominate cause of variability in results. The special anti-reflective area on the 2020 tubes allows more accurate turbidity readings for low NTU samples. Only 2020 tubes should be used with the 2020 turbidimeter. Orientation of the tube in the chamber will greatly affect the test results. To obtain the most accurate results, the tubes must be positioned so that the arrow-shaped index mark on the tube is aligned with the arrow-shaped index mark molded into the housing in front of the light chamber. This will ensure that the most accurate results are obtained.

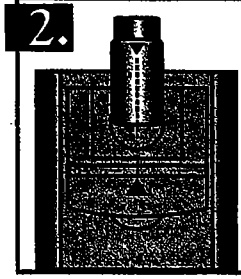


The 2020 turbidity tubes are optically selected but very small variations in the tubes may cause different readings on the same sample in low turbidity water. If greater accuracy is required, such as for Drinking Water requirements, the tubes supplied with the 2020 should be individually calibrated. This procedure is important for reading below 10 NTU but is probably not needed for samples above 10 NTU.

1. Fill each tube (0286) with high-quality water. (Generally distilled water or drinking water is sufficient.)



2. Record a turbidity reading for each tube following the instructions for turbidity measurement on page 19.

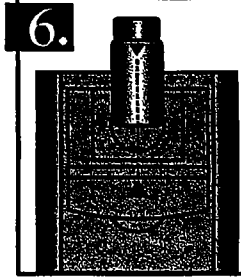


3. Mark the tube with the lowest reading with an "R", for reference turbidity tube, near the top of the tube with a permanent marker.

4. Follow the Calibration Procedure on page 17 using the reference turbidity tube, turbidity-free water, and the 1.00 NTU or 10.0 NTU AMCO™ standard.

5. Fill the remaining turbidity tubes with the same AMCO™ turbidity standard as in the reference turbidity tube.

6. Insert each tube into the meter with the proper orientation, Close lid and record the reading for each tube.



7. The difference between the theoretical value (1.00 NTU or 10.0 NTU) and the actual value is the correction factor for that tube. This factor should be used when comparing results from different tubes.

CALIBRATION

STANDARD SOLUTIONS

The 2020 has been pre-calibrated in the range of 0 to 1100 NTU with AMCO™ primary standards manufactured by Advanced Polymer Systems, Inc. This allows the 2020 to be used for treated water, natural water or wastewater. Recalibration of the 2020 by the user is not required. However, a procedure to standardize the calibration should be performed to obtain the most accurate readings over a narrow range.

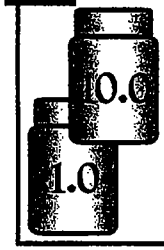
Two AMCO™ standards of 1.00 NTU and 10.0 NTU are supplied with the 2020. Standards of other values are available as accessories. The standards are a suspension of uniformly sized plastic "micro spheres" in ultra pure water, which require no preparation and are stable for long periods of time. These standards were manufactured specifically as a reference to calibrate the 2020. Only LaMotte specific AMCO™ standards should be used with the 2020. These standards are guaranteed to be accurate to within ±1%, if the following precautions are observed:

- The standards will remain stable for up to 4 years prior to opening if stored between 10 and 40°C.
- Once the seal of the bottle is broken, the stability of the standard is only guaranteed for 1 year if stored between 10 and 40°C.
- Never pour any unused or used standard back into the primary standard bottle.
- Do not open the bottle in a dusty or dirty environment. Dust and contaminants from the air can ruin the quality of the standard solutions.
- Before filling a tube with a standard, rinse the inside of the tube with a small amount of standard.
- Cap the standard bottle and the tube immediately after filling.

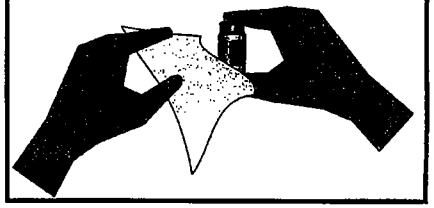
With proper preparation techniques, freshly prepared Formazin standards should be equivalent to the AMCO™ standards and can be used for meter calibration. A 4000 NTU Formazin Standard is available from LaMotte Company for use in preparing calibration standards. (See "Optional Accessories," pg. 6.) Correct procedures and approved methods for the use of Formazin standards can be found in the current edition of Standard Methods for Examination of Water and Wastewater.

CALIBRATION PROCEDURE

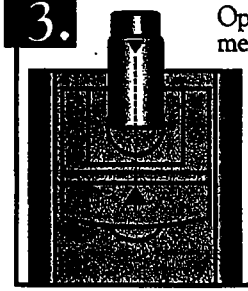
1. Select a LaMotte AMCO™ 2020 Standard in the range of the samples to be tested. NOTE: Only use LaMotte AMCO™ Standards specific to the 2020 Turbidimeterr. Contact LaMotte for replacement standards.



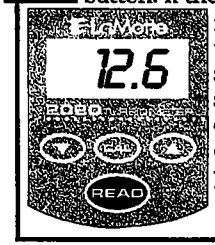
2. Fill a turbidity tube with the standard, cap, and wipe the tube clean with a lint-free cloth.



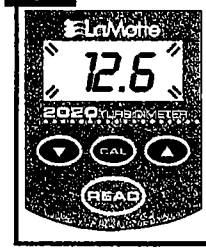
3. Open the lid of the meter. Align the indexing arrow mark on the tube with the indexing arrow mark on the meter, and insert the tube into the chamber.



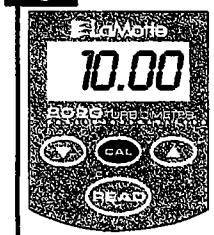
4. Close the lid. Push the **READ** button. If the displayed value is not the same as the value of the reacted standard (within the specification limits), continue with the calibration procedure.



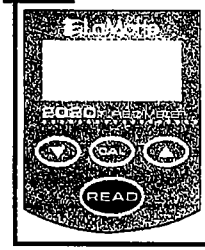
5. Push the **CAL** button for 5 seconds until **CAL** is displayed. Release button. The display will flash. Adjust the display with the ▼ and ▲ buttons until the value of the standard is displayed.



6. Push the **CAL** button again to memorize the calibration. The 2020 display will stop flashing. Calibration is complete.



7. Turn the unit off by holding the **READ** button down for at least 1 second, or proceed to measure the test samples following the procedure on page 19.



Note

The calibration procedure should be followed once a week, or more often as required by regulations and laws for compliance monitoring. The calibration of the meter is independent of the operating mode.

ANALYSIS PROCEDURES

SELECTING THE EPA MODE

The 2020 turbidity meter has two operating modes, the standard operating mode and the EPA mode. The meter can only be switched from one mode to the other while turning the 2020 on, from the OFF state. The 2020 will remain in which ever mode it was last used, even if the meter has been turned OFF.

To switch from one mode to the other mode:

1. Turn OFF the 2020, if it is on.

2. Press **CAL** button and hold it down while pressing the **READ** button to turn the meter on.

The meter will come on in the opposite mode than it was in previously. (While in EPA mode the ▲ will be visible on the display).

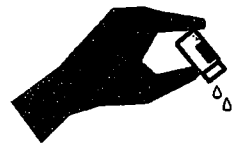
The standard operating mode displays the measured turbidity to the full resolution of the meter. The EPA mode displays the measured turbidity rounded to the reporting requirements of the EPA and Standard Methods compliance monitoring programs. This greatly simplifies the reporting requirements by eliminating the need for the user to manually round off the results according to EPA specifications. The EPA requires these reporting requirements because it recognizes the inherent accuracy of turbidity measurements within the specified ranges.

Note: The calibration of the meter is independent of the operating mode.

TURBIDITY MEASUREMENT

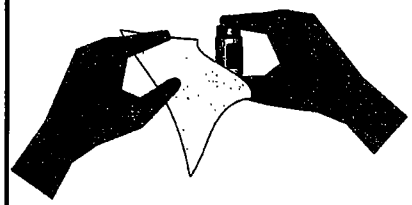
1. Fill a clean container with at least 50 mL of sample water and cover. Set sample aside to allow sample to equilibrate to air temperature and let gases escape. Avoid contaminants. Analyze as soon as possible.

2. Rinse an empty turbidity tube with a portion of the sample. Shake out excess water.



3. Fill the turbidity tube (0286) to the neck by carefully pouring the sample down the side of the tube to avoid creating bubbles.

4. Cap the tube and wipe tube dry with a clean lint-free tissue.



5. Open the 2020 lid. Align the indexing arrow on the tube with the indexing arrow on the meter. Insert the turbidity tube into chamber.

6. Close the lid. Push the **READ** button. The turbidity in NTU units will be displayed within 5 seconds.

7. The 2020 will turn off automatically 2 minutes after the last button push. To turn the meter OFF manually, hold the **READ** button down for at least 1 second. Release the button when OFF is displayed.

Note

If the sample is higher than 1100 NTU, it must be diluted and retested. See pages 20-22.

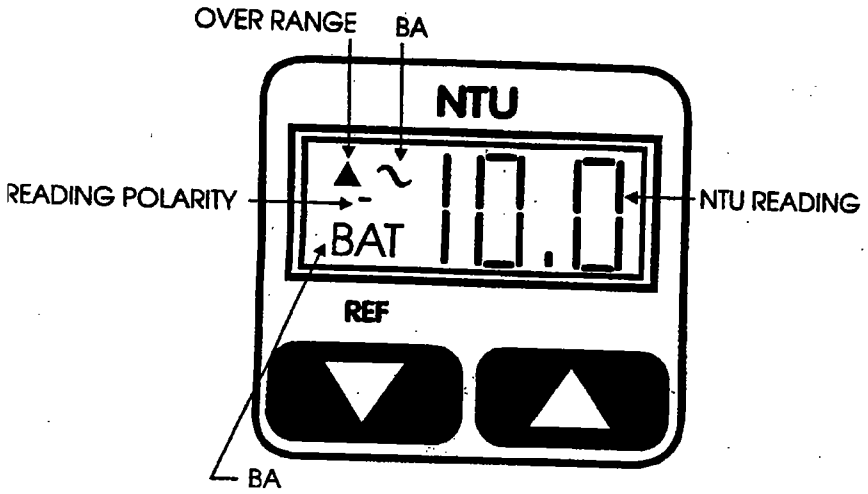
DRT-15CE
PORTABLE TURBIDIMETER
OPERATING & MAINTENANCE
MANUAL

HF scientific, inc.
3170 Metro Parkway
Fort Myers, FL 33916-7597
Phone: (813) 337-2116
FAX: (813) 332-7643

DRT-15CE (11/93)

PRE-OPERATION CHECK-OUT

Extreme care should be taken when handling the Reference Standard or sample cuvettes as surface scratches or finger smudges will cause analysis errors. Handle these items by the top only.



The battery, when new, usually requires several cycles of discharging and recharging in order to obtain optimum rated life between charges.

The turbidimeter provides up to 20 hours of continuous operation as a portable battery operated unit between recharges.

It is recommended that the unit be turned off between readings in order to obtain longer battery life between recharges. If used as a stationary unit leave the charger plugged in, but <u>TURN OFF INSTRUMENT WHEN NOT IN USE</u>. This will keep the battery at an optimum level at all times.

If for some reason the battery has been completely discharged, the display may not come "on" at all. If this happens turn the unit "off" and recharge the battery with the battery charger. To establish that the unit may be used while charging it, turn the unit on periodically and observe the lower left corner of the display for the word "BAT". When it goes off, (can no longer be seen while the rest of the display is on), the instrument may be used while the charger "tops off" the battery. Depending on the state of discharge of the battery, it may take as long as 6 - 8 hrs. to fully charge it. If the "BAT" indicator is "on", when the charger is not connected, the battery requires charging.

IV. OPERATION AND DESCRIPTION

To operate the turbidimeter, it is first necessary to standardize the instrument. Switch to the "10" range and place the Reference Standard (0.02 NTU) in the optical well.

The EPA recommends that cuvettes used for instrument calibration or sample measurement be indexed. For quick and repeatable indexing of the Reference Standard, an indexing ring and locator pin are included with this instrument.

When shipped, the white locator pin is installed in the collar ring around the optical well of your turbidimeter. The indexing ring is included in the accessory section of this instrument.

To index your Reference Standard, slowly rotate the Reference Standard, at least one complete revolution, while observing the reading, and locate the position of the lowest reading. Without moving the Reference Standard, install the indexing ring over the ridged cap of the Reference Standard, install the indexing ring over the ridged cap of the Reference Standard such that the notch on the ring aligns with the locator pin.

When indexing the Reference Standard in the future, simply insert the Reference Standard and rotate it until the notch on the indexing ring faces the locator pin. <u>Please note that this Reference Standard is only indexed to the turbidimeter for which it was aligned.</u>

To standardize, first index the Reference Standard as above. Then adjust the Reference Adjust in the appropriate direction to cause the display to read 0.02 NTU. The unit is now ready for use on any range.

To make a measurement of a sample, clean one of the cuvettes and fill it to within approximately 1/2" (12 mm) of the top with the sample to be measured. Place the cap on the cuvette and carefully clean the outside surface of the cuvette with a lint free wiper such as "Kimwipes". Place the sample in the well and take NTU reading directly from display. Select the appropriate range for best readability.

If the instrument has been subjected to cold (below 10 degrees Celsius) and then brought indoors, it should be allowed to warm up before use, since condensation may form on the various lenses. Warm up can be aided by leaving the case open and the instrument on for approximately a half hour.

V. RECORDER OUTPUT

The DRT-15CE has a 0-1 mA Recorder Output. The jack is located on right side of the chassis (refer to J2 on figure 2). To use, connect the 1/8" miniplug provided to your recorder. Adjust R17 (pot nearest jack) to obtain a full scale output compatible to a full scale reading on the DRT-15CE. Once this adjustment is made, the DRT-15CE will always be set up for this recorder. Use 10, 100 or 1000 NTU standard in appropriate range.

VI. CRITICAL MEASURING AREA

The critical measuring area of the sample cuvettes is the 3/4" wide band starting 5/8" above the bottom. Keep this area clean and free of scratches or abrasion. Handle by the top part only. (See Figure 1).

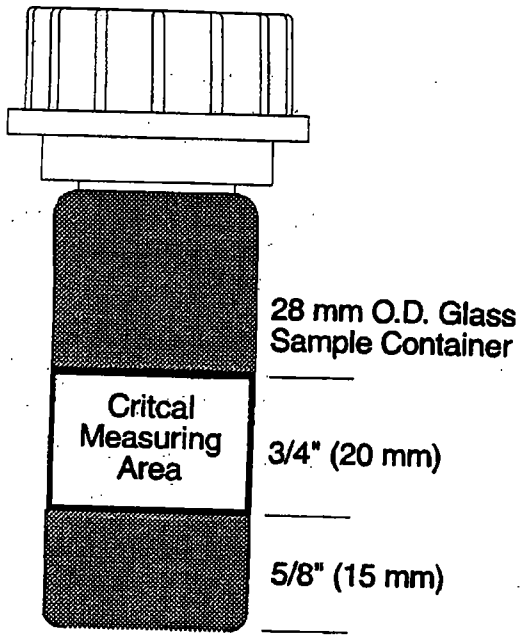


Figure 1

VII. CALIBRATION PROCEDURES

1. Calibration Standards

A. Secondary Standard Set (optional) Catalog No. 19071

HF Secondary Standards are recommended and certified by HF scientific. They are traceable to freshly prepared formazin primary standards. These standards are very easy to use off the shelf anytime without preparation making them an ideal turbidity standard. A Certificate of Traceability is available on request to HF scientific Customer Service Department. HF Secondary Standards may be used for calibration of HF turbidimeters. Order from HF scientific, inc.

NOTE: Do not freeze standards.
Do not leave standards in the measuring well for extended periods.
Do not shake standards.

Specific instructions for using certified Secondary Standards are included with the kit.

Each Secondary Standard Kit contains:
- -- Instructions
- -- 0.02 Reference Standard
- -- Certified Secondary Standards 10.00, 100.0, 1000 NTU Standards are contained in preselected cuvettes with light shield caps.
- -- A sturdy storage case

B. Standard Formazin Solutions

Calibration of this instrument is based on Formazin, a material which is made by polymerization.

Calibration samples may be obtained by diluting Formazin stock suspension using "Turbidity-Free" water. Formazin stock suspension can be prepared by the user (Reference Standard Methods For Examination of Water and Wastewater) or a kit can be purchased from, HF scientific, inc., Catalog No. 50040.

THE JOHNSON COMPANY, INC.
100 State Street, Suite 600
Montpelier, Vermont 05602
(802) 229-4600

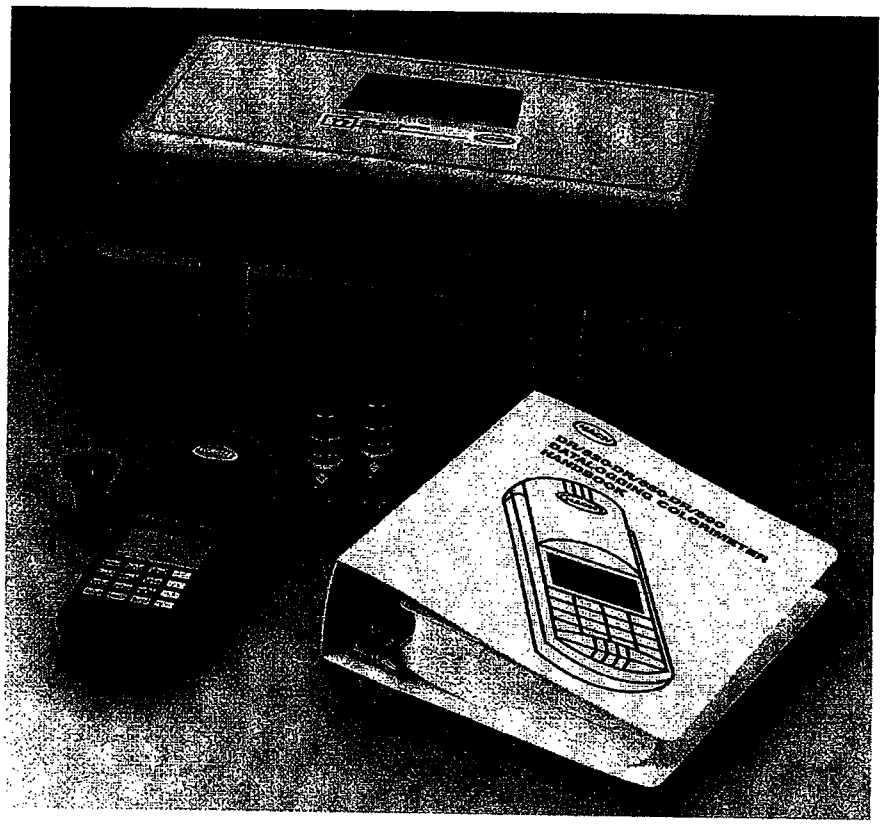
Attachment SSM-JCO-055-3

HACH DR690 Colorimeter Ferrous Iron Testing Instructions

(following 23 pages)

48470-22

DR/890
COLORIMETER
PROCEDURES MANUAL



te/dk 12/05 7ed

Using Sample Cells

Orientation of Sample Cells

Two round sample cells are shipped with the DR/820, DR/850 and DR/890. They are marked with 10-, 20- and 25-mL fill lines which may be used to measure the sample volume unless the procedure instructs you to use other glassware to measure the sample volume.

To minimize variability of measurements using a particular cell, always place the cell into the cell holder with the same orientation. The cells are placed in the instrument with the fill marks facing the user.

In addition to proper orientation, the sides of the cells should be free of smudges, fingerprints, etc. to ensure accurate readings. Wipe the sides of the cells with a moist cloth followed by a dry soft cloth to clean the surface before taking measurements.

Care of Hach Sample Cells

Store sample cells in their boxes when not in use to protect them from scratching and breaking. It is good laboratory practice to empty and clean sample cells after analyses are complete--avoid leaving colored solutions in the cells for extended periods of time. Finish the cleaning procedure with a few rinses of deionized water and allow to dry. Individual procedures often recommend specific cleaning methods.

Cleaning Sample Cells

Most laboratory detergents can be used at recommended concentrations. Neutral detergents such as Neutracon are safer if regular cleaning is required, as in the case of protein residues.

If using a detergent, you can speed cleaning by increasing the temperature or using an ultrasonic bath.

Rinsing is more efficient when using deionized water.

Using the COD/TNT Adapter

Use care when seating a vial into the COD/ TNT adapter (for COD vials and Test 'N Tubes). Place the vial into the adapter and press straight down on the top of the vial until it seats solidly. Do not move the vial from side to side; this can cause errors.

Volume Measurement Accuracy

The sample cells supplied with the instrument have fill marks to indicate 10, 20 or 25 mL. The fill marks are intended to measure the volume to be analyzed. Do not use these fill marks to perform sample dilutions.

If a sample must be diluted, use a pipet, graduated mixing cylinder and/or a volumetric flask for accurate measurement. When diluting, accuracy is important because a slight mistake in measuring a small sample will cause

a substantial error in the result. For instance, a 0.1-mL mistake in the dilution of a 1.0-mL final volume produces a 10% error in the test result.

Volumes for standard additions can be measured using the 25-mL mark, but it is not recommended for the 10-mL mark due to a potentially excessive relative error. An error of 0.5 mL in 25 mL is only 2%, while 0.5 mL error in 10 mL is 5%.

For 10 mL standard additions, follow this procedure:

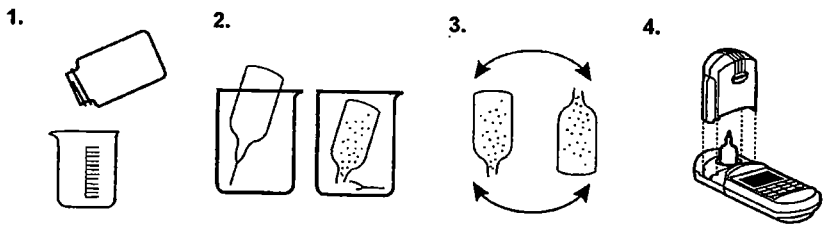
1. Transfer 10.0 mL of sample into a clean, dry sample cell (the unspiked sample).
2. Add the standard (spike) to a 25 mL portion of sample in a 25-mL mixing cylinder. Stopper and mix thoroughly.
3. Transfer 10 mL to another sample cell (use fill mark) for analysis.

Using AccuVac Ampuls

AccuVac ampuls contain pre-measured powder or liquid in optical-quality glass ampuls.

1. Collect the sample in a beaker or other open container.
2. Place the ampul tip well below the sample surface and break the tip off (see *Figure 6*) against the beaker wall. The break must be far enough below the surface to prevent air from being drawn in as the level of the sample lowers (the AccuVac Breaker may be used instead of breaking the ampul against the beaker side).
3. Invert the ampul several times to dissolve the reagent. Do not place your finger over the broken end; the liquid will stay in the ampul when inverted. Wipe the ampul with a towel to remove fingerprints, etc.
4. Insert the ampul into the instrument and read the results directly.

Figure 6 Using AccuVac Ampuls



Temperature Considerations

For best results, perform most tests in this manual with sample temperatures between 20 °C (68 °F) and 25 °C (77 °F). If a test requires closer temperature control, notes in the procedure will indicate this.

Sample Dilution Techniques

Ten and 25 mL are the volumes used for most colorimetric tests. However, in some tests, the color developed in the sample may be too intense to be measured. Unexpected colors may develop in other tests. In both cases, dilute the sample to determine if interfering substances are present.

To dilute the sample easily, pipet the chosen sample portion into a clean graduated cylinder (or volumetric flask for more accurate work). Fill the cylinder (or flask) to the desired volume with deionized water. Mix well. Use the diluted sample when running the test.

To help with dilutions, *Table 5* shows the amount of sample used, the amount of deionized water used to bring the volume up to 25 mL and the multiplication factor.

The concentration of the sample is equal to the diluted sample reading multiplied by the multiplication factor.

More accurate dilutions can be done with a pipet and a 100-mL volumetric flask (see *Table 6* for more information). Pipet the sample and dilute to volume with deionized water. Swirl to mix.

Table 5 Sample Dilution Volumes

Sample Volume (mL)	mL Deionized Water Used to Bring the Volume to 25 mL	Multiplication Factor
25.0	0.0	1
12.5	12.5	2
10.0[1]	15.0	2.5
5.0[1]	20.0	5
2.5[1]	22.5	10
1.0[1]	24.0	25
0.250[1]	24.75	100

[1] For sample sizes of 10 mL or less, use a pipet to measure the sample into the graduated cylinder or volumetric flask.

Table 6 Multiplication Factors for Diluting to 100 mL

Sample Volume (mL)	Multiplication Factor
1	100
2	50
5	20
10	10
25	4
50	2

Sample Dilution and Interfering Substances

Sample dilution may influence the level at which a substance may interfere. The effect of the interferences decreases as the dilution increases. In other words, higher levels of an interfering substance can be present in the original sample if it is diluted before analysis.

An Example:

Copper does not interfere at or below 100 mg/L for a 25.00 mL sample in a procedure. If the sample volume is diluted with an equal volume of water, what is the level at which copper will not interfere?

$$\frac{\text{Total volume}}{\text{Sample volume}} = \text{Dilution factor}$$

$$\frac{25}{12.5} = 2$$

Interference Level × Dilution Factor = Interference level in sample

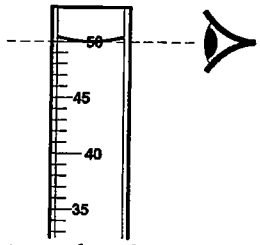
$100 \times 2 = 200$

The level at which copper will not interfere in the undiluted sample is at or below 200 mg/L.

Using Pipets and Graduated Cylinders

When small sample quantities are used, the accuracy of measurements is important. *Figure 3* illustrates the proper way of reading the sample level or the meniscus formed when the liquid wets the cylinder or pipet walls.

Figure 3 Reading the Meniscus



Rinse the pipet or cylinder two or three times with the sample to be tested before filling. Use a pipet filler or pipet bulb to draw the sample into the pipet. Never pipet chemical reagent solutions or samples by mouth. When filling a pipet, keep the tip of the pipet below the surface of the sample as the sample is drawn into the pipet.

Serological pipets have marks that indicate the volume of liquid delivered by the pipet. The marks may extend to the tip of the pipet or may be only on the straight portion of the tube. If the marks are only on the straight part of the tube, fill serological pipets to the zero mark and discharge the sample by draining the sample until the meniscus is level with the desired mark. If the serological pipet has marks extended to the tip of the pipet, fill the pipet to the desired volume and drain all the sample from the pipet. Then blow the sample out of the pipet tip for accurate measurements.

Volumetric (transfer) pipets have a bulb in the middle and a single ring above the bulb to indicate the volume of liquid when it is filled to the mark. To discharge a volumetric pipet, hold the pipet vertical until only a small amount of liquid remains (about ¾ inch), then hold the pipet at a slight angle against the container wall to drain. Do not attempt to discharge the solution remaining in the tip of the pipet after draining. Volumetric pipets are designed to retain a small amount of sample in the pipet tip.

If sample drops stay on the walls of the pipet, the pipet is dirty and is not delivering the correct amount of sample. Wash the pipet thoroughly with a laboratory detergent or cleaning solution and rinse several times with deionized water.

Using the TenSette Pipet

For best results use a new tip each time you pipet. After several uses, the pipet tip may retain some liquid, causing inaccurate delivery. Each pipet is supplied with 50 tips; order Hach replacement tips for best results.

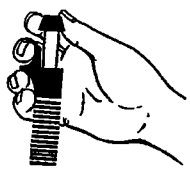
Always use careful, even hand movements for best reproducibility. If the pipet does not operate smoothly, disassemble and coat the piston and retainer with high-quality stopcock grease. Also coat the metering turret lightly with grease. Refer to the TenSette Pipet manual.

For best pipetting accuracy, the solution and the room temperature should be between 20-25 °C.

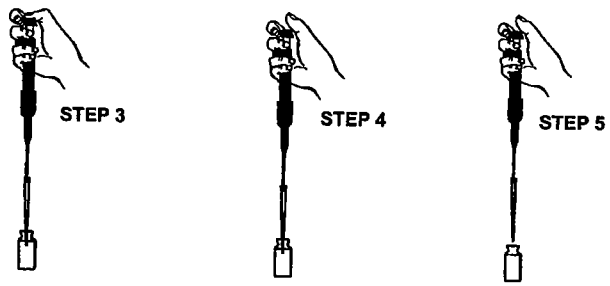
Never lay the pipet down with the liquid in the tip. Solution could leak into the pipet and cause corrosion.

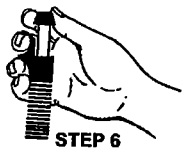
Operating the TenSette Pipet

1. Attach a clean tip by holding the pipet body in one hand and gently pressing the large end of the pipet tip onto the tapered end of the pipet. Be sure a good seal is obtained.



2. Turn the turret cap to align the desired volume with the mark on the pipet body.
3. Using a smooth motion, press down on the turret cap until it reaches the stop. Immerse the tip about 5 mm (¼ inch) below the solution surface to avoid drawing air into the pipet. Do not insert the tip any deeper or the delivery volume may be affected.
4. While maintaining a constant pressure, allow the turret to return slowly to the extended position. A rapid return may affect the delivery volume.
5. With the turret up, take the tip out of the solution and move it to the receiving vessel. Do not press on the turret cap while moving the pipet.




STEP 6

6. Use the thumb and forefinger to twist the turret cap to the next higher volume position to ensure quantitative transfer of the sample. The "F" position provides full blowout.


STEP 7

7. With the tip in contact with the side of the receiving vessel, slowly and smoothly press down on the turret cap until it reaches the stop and the solution is completely discharged.

Mixing Water Samples

The following two methods may be helpful in tests that require mixing sample with chemicals (usually indicated by "invert to mix" instructions).

1. When mixing sample in a round sample cell or mixing cylinder, invert the cell or cylinder; see *Figure 4*. Hold the cell in a vertical position with the cap on top. Invert the cell so the cap is on the bottom. Return the cell to the original position. Do the same with the mixing cylinder.

2. Swirling is recommended when mixing samples in a graduated cylinder or a titration flask. Grip the cylinder (or flask) firmly with the tips of three fingers; see *Figure 5*. Hold the cylinder at a 45-degree angle and twist the wrist. This should move the cylinder in an approximately 12-inch circle, creating enough rotation to complete the mixing in a few turns.

These mixing procedures are the most gentle. Both methods are simple but take a bit of practice to obtain the best results.

Figure 4 Inverting a Sample Cell

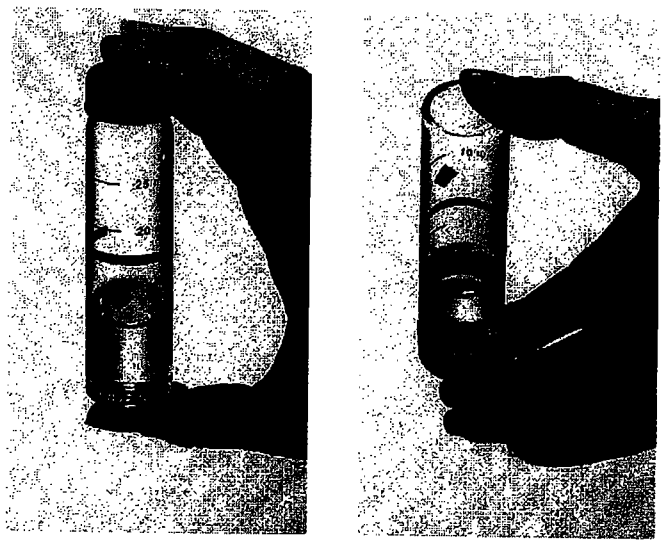
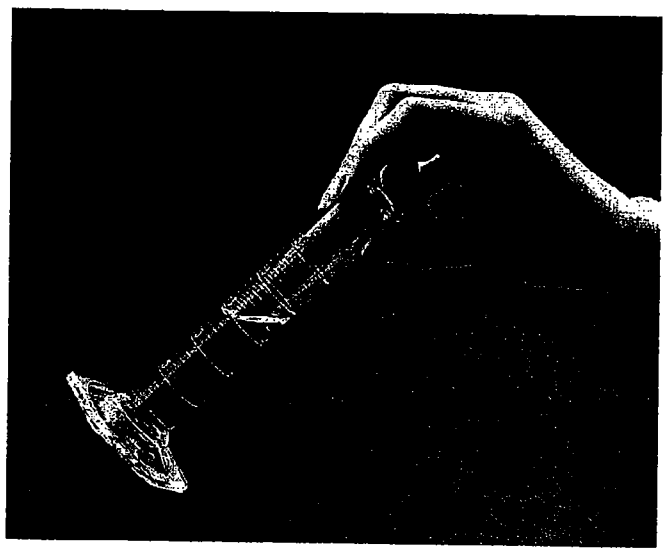


Figure 5 Swirling a Graduated Cylinder



If you are using a Reagent Blank Correction, the blank correction should be entered before the standard curve is adjusted.

To adjust the standard curve:

1. Prepare the standard.
2. Use the standard as the sample in the procedure.
3. When the reading for the standard is obtained, press **SETUP**.
4. Use the arrow keys to scroll to the "**STD**" setup option.
5. Press **ENTER** to activate the standard adjust option.
6. Edit the standard concentration to match that of the standard used.
7. Press **ENTER**. A small plot of a line through a point will be displayed, indicating that the curve has been adjusted with the standard.

Note: *If the attempted correction is outside the allowable adjustment limit, the instrument will beep and flash Ø and the operation will not be allowed.*

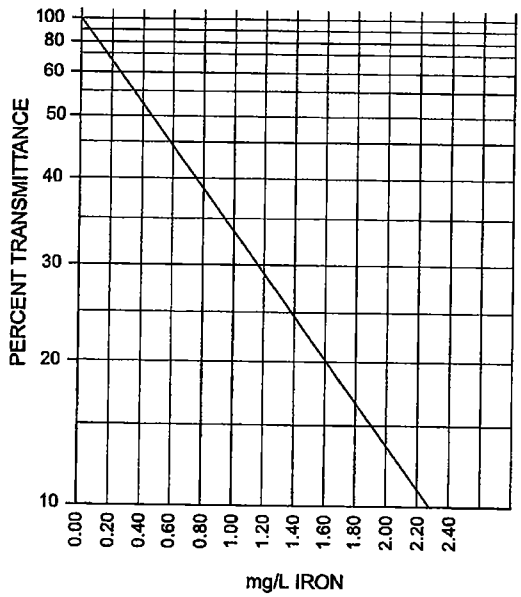
Preparing a User-Entered Calibration Curve

1. Prepare five or more standards of known concentration that cover the expected range of the test. Run tests as described in the procedure on each prepared standard. Pour the customary volume of each known solution into a separate clean sample cell of the type specified for your instrument.
2. Standardize (zero) the instrument using an untreated water sample or a reagent blank, whichever the procedure instructs you to use.
3. Measure and record the absorbance or %T of the known solutions. To use %T vs. concentration see *%T Versus Concentration Calibration.* To use absorbance vs. concentration, see *Absorbance Versus Concentration Calibration.* Or create a user-entered program by storing a custom calibration in the non-volatile memory of the instrument. Refer to the section on entering user-entered programs in the instrument manual.

%T Versus Concentration Calibration

If measuring %T, use semilogarithmic graph paper and plot %T (vertical scale) versus concentration (horizontal scale). In *Figure 11*, iron standard solutions of 0.1, 0.2, 0.4, 0.8, 1.2, 1.6, and 2.0 mg/L were measured on a spectrophotometer at 500 nm using half-inch test tubes. Results were plotted and the calibration table values were extrapolated from the curve (*Table 7*).

Figure 11 Logarithmic Calibration Curve



To convert %T readings to concentration, prepare a table such as *Table 7* and select the appropriate line from the "%T Tens" column and the appropriate column from the %T Units columns. The %T Ten value is the first number of the %T reading and the %T Units value is the second number of the %T reading. For example, if the instrument reading was 46%, the 40 line in the %T Tens column and the 6 column in the %T Units would be selected. The cell where these two intersect (0.78 mg/L) is the iron concentration of the sample.

Table 7 Calibration Table

%T Tens	%T Units									
	0	1	2	3	4	5	6	7	8	9
0										
10	2.30	2.21	2.12	2.04	1.97	1.90	1.83	1.77	1.72	1.66
20	1.61	1.56	1.51	1.47	1.43	1.39	1.35	1.31	1.27	1.24
30	1.20	1.17	1.14	1.11	1.08	1.04	1.02	.99	.97	.94
40	.92	.89	.87	.84	.82.	.80	.78	.76	.73	.71
50	.69	.67	.65	.64	.62	.60	.58	.56	.55	.53
60	.51	.49	.48	.46	.45	.43	.42	.40	.39	.37
70	.36	.34	.33	.32	.30	.29	.28	.26	.25	.24
80	.22	.21	.20	.19	.17	.16	.15	.14	.13	.12
90	.11	.09	.08	.07	.06	.05	.04	.03	.02	.01

Absorbance Versus Concentration Calibration

To read concentration values directly from the instrument, create a user-entered program. See the instrument manual for more information.

If absorbance values are measured, plot the results on linear graph paper. Plot the absorbance value on the vertical axis and the concentration on the horizontal axis.

Plot increasing absorbance values from bottom to top. Plot increasing concentration values from left to right. Values of 0.000 absorbance units and 0 concentration will begin at the bottom left corner of the graph. A calibration table can be extrapolated from the curve or the concentration values can be read directly from the graph for determining an equation for the line using the slope and the y-intercept.

USEPA Approved and Accepted Definitions

The United States Environmental Protection Agency (USEPA) establishes limits for maximum contamination levels of certain constituents in water. It also requires that specific methodology be used to analyze for these constituents. These methods originate from several sources. The USEPA has developed some of these methods. In other cases, the USEPA has evaluated and approved methods developed by manufacturers, professional groups and public agencies such as:

- American Public Health Association

- American Water Works Association
- Water Environmental Federation
- American Society for Testing and Materials
- United States Geological Survey
- Associates of Official Analytical Chemists

All USEPA approved methods are cited in the *Federal Register* and compiled in the Code of Federal Regulations. USEPA approved methods may be used for reporting results to the USEPA and other regulatory agencies.

USEPA Accepted

Hach has developed several procedures that are equivalent to USEPA approved methods. Even though minor modifications exist, the USEPA has reviewed and accepted certain procedures for reporting purposes. These methods are not published in the *Federal Register,* but are referenced to the equivalent USEPA method in the procedure.

SECTION 4 CREATING USER-ENTERED PROGRAMS

⚠ *DANGER*
This instrument is not intended for use with flammable samples or those containing hydrocarbons.

PELIGRO
Este instrumento no está destinado para uso con muestras inflamables o que contengan hidrocarburos.

PERIGO
Este instrumento não é feito com o fim de ser empregado com amostras inflamáveis ou aquelas que contêm hidrocarbonetos.

DANGER
Cet instrument n'est pas conçu pour une utilisation avec des échantillons inflammables ou des échantillons contenant des hydrocarbures.

GEFAHR
Dieses Gerät darf nicht für Tests mit brennbaren Proben oder Proben, die Kohlenwasserstoffe enthalten, benutzt werden.

The DR/800 Series Colorimeters can store the calibration information needed to read prepared samples from up to five different user-entered programs. To create a new, user-entered program, you will need a blank and prepared standards or the correct absorbance readings for each standard. The prepared standards are made with standard solutions of the parameter (i.e. analyte). Up to twelve concentrations of standards, including a zero concentration standard, may be used.

The absorbances of the prepared standards must be different from one another. If the colorimeter detects a duplicate, it will beep and ignore the latest reading.

Using a previously entered method's program number erases all the previously entered information stored under that program number.

While creating a user-entered program, the colorimeter remains on for four hours following any keypress. If more than four hours pass between keypresses, the instrument will power down. All data which was entered, but not yet stored, will be deleted. The user-entered program must be re-entered from the beginning.

SI

4.1 User-Entered Programs

The instrument allows storage of up to five user-entered programs (101-105) and up to 113 Hach programs.
A minimum of two data points are required for the instrument to recognize and accept a user-entered program.

- Program numbers 101 through 105 are reserved for storing user-entered programs.
- The maximum number of data points that can be entered for a method is 12. After the twelfth standard (1 through 12) is accepted, the instrument stores the method and will not accept any more data, but will allow the user to review the data already entered.

Before entering a calibration, determine the optimum wavelength, timing sequences (if any), and the workable range of the method.

4.4

4.2 Calibration Curves

Calibration curves may have positive or negative slopes, but they must be based on absorbance (% transmittance not allowed) and must pass through the origin that represents zero concentration.

It is important that the standards adequately describe the curve over the range of interest. Because this is largely dependent on the shape of the curve, it may be necessary to prepare a preliminary curve using extra data points to help select the appropriate standards.

If the curve is linear, only two concentration data points are needed. For example, standards with a zero absorbance and a standard with 1.000 absorbance are appropriate. If the curve is nonlinear, additional data points are needed to achieve good accuracy. Up to 12 data points can be entered for a single calibration curve.

4.3 User-entered Program Information for Bleaching Chemistries

Although the majority of colorimetric test procedures produce a higher absorbance (i.e. deeper color) as the concentration of the parameter being measured increases, some tests do the opposite. These bleaching chemistries (fluoride is one example) produce a lighter color at increasing concentrations. The zero concentration

standard is usually produced by combining deionized water with the reagents. Commonly this solution is used to zero the instrument as in Step *step 14* of *Section 4.4 Creating a New User-entered Program.*

Once the zero is entered, the prepared standards must be read from lightest to darkest. In the case of bleaching chemistries, the absorbance values reported by the colorimeter may be negative.

Even when your test produces a lower absorbance (lighter color) with increasing concentration, the prepared standards must be read by the colorimeter in the order of increasing absorbance (i.e., from colorless or the palest color, to the deepest color). The instrument will not accept standards read out of order.

4.4 Creating a New User-entered Program

Use the step-by-step instructions below to enter a new user-entered program into instrument memory. Terminate at any point (before the program is stored) by pressing the **EXIT** key until the display is blank. The colorimeter will not retain any of the entered data.

1. Press the **I/O** key to turn on the instrument.
2. Press the **SETUP** key. The display will show SETUP in the upper-left and the down-arrow icon in the lower-right. Available action functions are also shown.
3. Press the down **ARROW** key until USER is displayed.
4. Press the up **ARROW** key if the display goes past USER.
5. Press the **ENTER** key. Four horizontal lines (numeric entry display) will be displayed.
6. Select a program number from 101 through 105 by pressing the corresponding digit key. The number will appear in the display.

Note: *Press* **CE** *to correct errors.*

7. Press **ENTER**. A wavelength and nm will be displayed.

- If the wavelength is correct as displayed, skip to Step *step 8.*
- Some instrument models can use different wavelengths. If a different wavelength is preferred, proceed as follows:

a. Press **ENTER**. A flashing question mark will be displayed in the lower-right corner.

b. Press either **ARROW** key until the preferred wavelength is displayed.

c. Press **ENTER** to accept the displayed wavelength. The down-arrow icon will be displayed.

8. Press the down **ARROW** key to move to the **RES** (resolution) option. One to four zeros, a decimal point if needed, and the units of concentration may be modified here.

- If the displayed resolution and units are correct, skip to step *step 9.*
- If the displayed resolution or units are incorrect for your test, proceed with the following:

a. Press **ENTER**. A flashing question mark will be displayed.

b. Press either **ARROW** key until the preferred resolution and concentration units are displayed. The available options are:

0.000	0.00	0.0	0
0.000 µg/L	0.00 µg/L	0.0 µg/L	0 µg/L
0.000 mg/L	0.00 mg/L	0.0 mg/L	0 mg/L
0.000 g/L	0.00 g/L	0.0 g/L	0 g/L

c. Press **ENTER**. The question mark will disappear.

9. Press the down **ARROW** key to scroll to **STD**. **STD** and the number of the standard (i.e., 1 is shown for the first standard, 2 for the second, etc.) will be shown on the lower portion of the display.

10. Press **ENTER**. Four horizontal lines (denoting numeric entry) will be displayed.

11. Enter the standard's concentration, using the numeric entry keys (the # icon will be illuminated on the display).

Note: Press the **CE** *key to correct errors.*

12. Press the **ENTER** key. The concentration will be displayed.

Note: A beep means that the concentration is a duplicate of a previous standard or the concentration is too high for the selected resolution. Repeat step step 11 with a different concentration and continue.

13. Press the down **ARROW** key. **ABS** will be displayed followed by the number of the standard.

14. The colorimeter requires one zero be entered in this procedure; the **ZERO** action icon will appear in the lower portion of the display. Place a blank into the cell holder and press the **ZERO** key. Four horizontal lines will appear, then disappear, across the display. The **READ** action icon will appear in the lower portion of the display.

Note: If necessary, the colorimeter can be re-zeroed. The most recently entered zero will be used for subsequent readings.

15. Prepare the standards using the same reagents and procedure used to test samples.

16. Place the prepared standard into the cell holder.

17. Press the **READ** key. An absorbance value will be displayed.

Note: Or, press the **ENTER** *key to input an absorbance value or change the value read by the instrument. Use the numeric keys to enter the value then press the* **ENTER** *key.*

Note: A beep indicates that the absorbance is a duplicate of a previously entered standard or that it falls between two previous standards. Repeat steps step 15 through 17. with the correct standard, or press the up **ARROW** *key and repeat steps 9. through 17. with a correct, prepared standard and blank.*

18. Press the down **ARROW** key to advance to the next standard.

19. Repeat steps *step 9* through *step 18* for all remaining standards.

20. Press the **EXIT** key once. **STORE ?** will be displayed.

21. Press the **ENTER** key to store the new method in the instrument's memory.

4.5 Reviewing and Editing User-Entered Programs

Note: When a user-entered program is edited and stored, all stored data associated with that program is erased.

All method information previously stored by the operator can be reviewed and changed to add, delete, or modify data points. At any point during the editing function, the operator can terminate the procedure and exit by pressing the **EXIT** key. No changes to the program will occur.

Because the standards must be read in the order of increasing absorbancy, data points may not be inserted into the middle of an existing user-entered program.

To review and edit previously stored user-entered programs:

1. Press the **I/O** key to turn the instrument on.
2. Press the **SETUP** key.
3. Scroll to the **USER** option and press **ENTER**.
4. Enter the program number of the method to review or edit and press the **ENTER** key.
5. Scroll through the calibration information using the **ARROW** keys. To avoid making changes, press the **EXIT** key.
6. To edit the data shown on the display, press **ENTER**. Make necessary changes, then press the **ENTER** key to return to reviewing the data.
7. Press **EXIT** once. **STORE?** will be displayed.
8. Press **ENTER** to store the program.

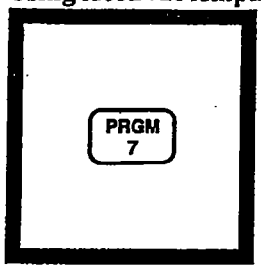
4.6 Erasing User-entered Programs

Note: When a user-entered program is erased, all stored data associated with that program is also erased.

User-entered programs are automatically deleted when another user-entered program is entered and stored in the previously entered method's storage number (101-105). They also may be erased from the instrument memory as follows:

1. Press the **I/O** key to turn the instrument on.
2. Press the **SETUP** key.
3. Scroll to the **USER** option and press **ENTER**.
4. Enter the program number of the method to be erased and then press **ENTER**.
5. Scroll to the concentration data for STD 1 using the down **ARROW** key. Press **ENTER**.
6. Press **CE**. Press **ENTER**.
7. Press the **EXIT** key. **ERASE?** will be displayed.
8. Press the **ENTER** key to erase the method or the **EXIT** key to retain it in memory.

Using AccuVac Ampuls



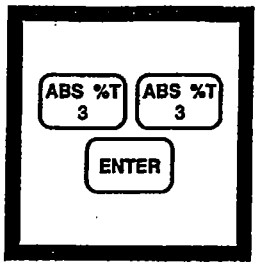
1. Enter the stored program number for ferrous iron (Fe^{2+}) AccuVac ampuls.

Press: **PRGM**

The display will show:

PRGM ?

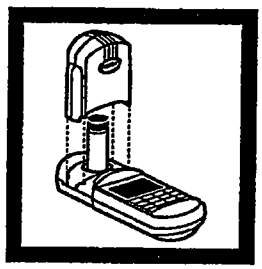
***Note:** Analyze samples as soon as possible to prevent air oxidation of ferrous iron to ferric, which is not determined.*



2. Press: **33 ENTER**

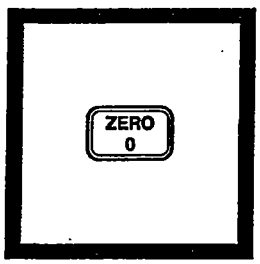
The display will show **mg/L, Fe** and the **ZERO** icon.

3. Fill a sample cell with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50-mL beaker.



4. Place the blank into the cell holder. Tightly cover the sample cell with the instrument cap.

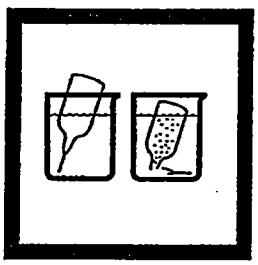
IRON, FERROUS, continued



5. Press: **ZERO**

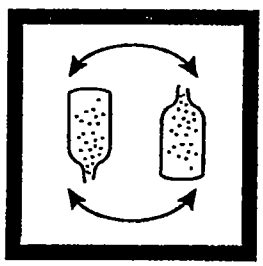
The cursor will move to the right, then the display will show:

0.00 mg/L Fe



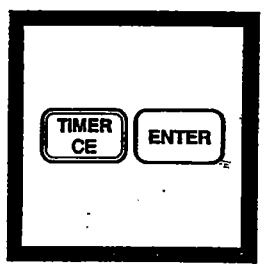
6. Fill a Ferrous Iron AccuVac Ampul with sample.

***Note:** Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

***Note:** Undissolved powder does not affect accuracy.*

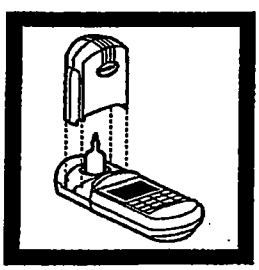


8. Press:

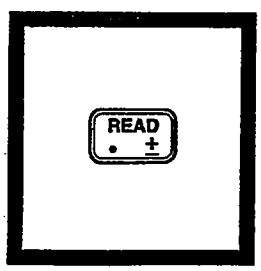
TIMER ENTER

A three-minute reaction period will begin.

***Note:** An orange color will form if ferrous iron is present.*



9. Place the AccuVac ampul into the cell holder. Tightly cover the sample cell with the instrument cap.



10. Press: **READ**

The cursor will move to the right, then the result in mg/L ferrous iron will be displayed.

***Note:** Standard Adjust may be performed using a prepared standard (see Standard Adjust in Section 1).*

IRON, FERROUS, continued

REQUIRED REAGENTS & APPARATUS (USING POWDER PILLOWS)

Description	Quantity Required Per Test	Units	Cat. No.
Ferrous Iron Reagent Powder Pillows	1 pillow	100/pkg	1037-69
Sample Cell, 10-20-25 mL, w/ cap	2	6/pkg	24019-06

REQUIRED REAGENTS & APPARATUS (USING ACCUVAC AMPULS)

Ferrous Iron Reagent AccuVac Ampuls	1 ampul	25/pkg	25140-25
Beaker, 50 mL	1	each	500-41

OPTIONAL REAGENTS

Ferrous Ammonium Sulfate, hexahydrate, ACS		113 g	11256-14
Water, deionized		4 L	272-56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Balance, analytical, 115 V	each	26103-00
Balance, analytical, 230 V	each	26103-02
Clippers, for opening powder pillows	each	968-00
Flask, volumetric, 100 mL, Class A	each	14574-42
Flask, volumetric, 1000 mL, Class A	each	14574-53
Pipet, volumetric, Class A, 1.00 mL	each	14515-35
Pipet Filler, safety bulb	each	14651-00
Weighing Boat, 67/46 mm, 8.9 cm square	500/pkg	21790-00

For Technical Assistance, Price and Ordering
In the U.S.A.—Call 800-227-4224
Outside the U.S.A.—Contact the Hach office or distributor serving you.

Total Alkalinity Titrets® 10 - 100 ppm

Test Procedure

1. Fill the sample cup to the 20 mL mark with your sample (fig. 1).
2. Add 6 drops of A-9800 Activator Solution to the sample (fig. 2). Stir briefly to mix the contents of the sample cup.
   NOTE: The sample should now be green. If it is pink, total alkalinity is 0 ppm. There is no need to continue.
3. Gently snap the tip of the glass ampoule at the white ring nearest the end of the tapered tip (fig. 3).
   NOTE: When the tip is snapped, the flexible tubing will remain in place on the tapered neck of the ampoule.
4. Lift the control bar and insert the Titret assembly into the Titrettor (fig. 4).
   NOTE: The rigid sample pipe will extend approximately 1.5 inches beyond the body of the Titrettor.
5. Hold the Titrettor with the sample pipe in the sample and press the control bar firmly, but briefly, to pull in a small amount of sample. The contents will turn a **PINK** color (fig. 5).
   NOTE: NEVER press the control bar unless the sample pipe is immersed in the sample.
6. With the sample pipe in the sample, press the control bar again briefly to allow another small amount of sample to be drawn into the ampoule.

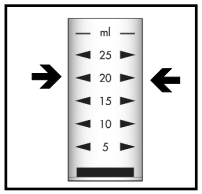


Figure 1

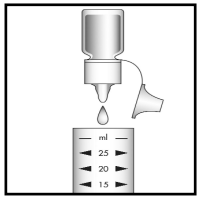


Figure 2

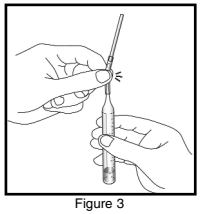


Figure 3

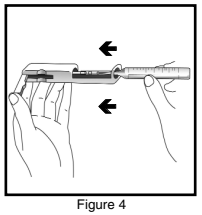


Figure 4

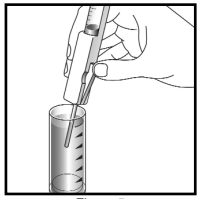


Figure 5

7. After each addition, rock the entire assembly to mix the contents of the ampoule. Watch for a color change from **PINK to BRIGHT GREEN**.
8. Repeat steps 6 and 7 until a permanent color change occurs.

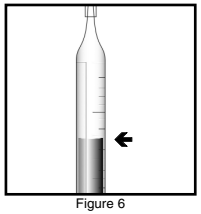


Figure 6

9. When the color of the liquid in the ampoule changes to **GREEN**, remove the ampoule from the Titrettor. Hold the ampoule in a vertical position and read the scale opposite the liquid level (fig. 6). Results are expressed in ppm (mg/Liter) calcium carbonate ($CaCO_3$).

Test Method

The Total Alkalinity Titrets®[1] test method employs an acid titrant and a mixed pH indicator.[2,3,4] Results are expressed as calcium carbonate ($CaCO_3$).

1. Titrets is a registered trademark of CHEMetrics, Inc. U.S. Patent No. 4,332,769
2. ASTM D 1067 - 92 (1996), Acidity or Alkalinity of Water
3. APHA Standard Methods, 20th ed., p. 2-27, method 2320 B (1998)
4. EPA Methods for Chemical Analysis of Water and Wastes, method 310.1 (1983)

Safety Information

Read MSDS before performing this test procedure. Wear safety glasses.

Reorder Information **Cat. No.**

***Test Kit**, complete* *K-9810*

Kits are available for total alkalinity analysis at other levels.

CHEMetrics, Inc., 4295 Catlett Road, Calverton, VA 20138-0214 U.S.A.
Phone: (800) 356-3072; Fax: (540) 788-4856; E-Mail: orders@chemetrics.com
0492-7

Carbon Dioxide Titrets®
10 - 100 ppm

Test Procedure

1. Fill the sample cup to the 20 mL mark with your sample (fig. 1).
2. Add 2 drops of A-1900 Activator Solution to the sample (fig. 2). Stir briefly to mix the contents of the sample cup.

   NOTE: If the sample turns pink, carbon dioxide is 0 ppm. There is no need to continue.
3. Gently snap the tip of the glass ampoule at the white ring nearest the end of the tapered tip (fig. 3).

   NOTE: When the tip is snapped, the flexible tubing will remain in place on the tapered neck of the ampoule.
4. Lift the control bar and insert the Titret assembly into the Titrettor (fig. 4).

   NOTE: The rigid sample pipe will extend approximately 1.5 inches beyond the body of the Titrettor.
5. Hold the Titrettor with the sample pipe in the sample and press the control bar firmly, but briefly, to pull in a small amount of sample. The contents will turn a **PINK** color (fig. 5).

   NOTE: NEVER press the control bar unless the sample pipe is immersed in the sample.
6. With the sample pipe in the sample, press the control bar again briefly to allow another small amount of sample to be drawn into the ampoule.

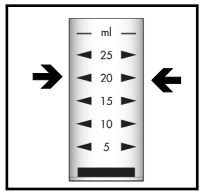


Figure 1

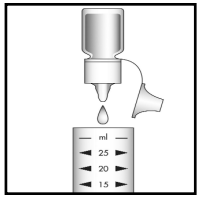


Figure 2

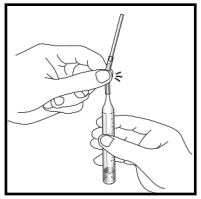


Figure 3

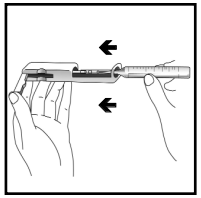
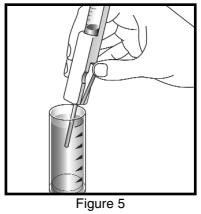


Figure 4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7. After each addition, rock the entire assembly to mix the contents of the ampoule. Watch for a color change from **PINK to COLORLESS**.
8. Repeat steps 6 and 7 until a permanent color change occurs.

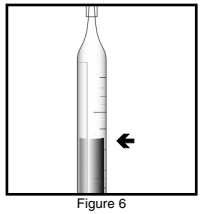
Figure 6

9. When the color of the liquid in the ampoule changes to **COLORLESS**, remove the ampoule from the Titrettor. Hold the ampoule in a vertical position and read the scale opposite the liquid level (fig. 6). Results are expressed in ppm (mg/Liter) carbon dioxide as CO_2.

Test Method

The Carbon Dioxide Titrets®[1] test method employs a caustic titrant with pH indicator method.[2,3] Results are expressed in ppm (mg/Liter) carbon dioxide as CO_2. Sulfide will not interfere up to 0.4 ppm. However if the sulfide concentration is >0.4 ppm, the following formula is used to calculate the volume of A-1905 Neutralizer solution that should be added to 20 mL of the sample prior to performing the Test Procedure:

mL of A-1905 Solution = ppm sulfide ÷ 10

1. Titrets is a registered trademark of CHEMetrics, Inc. U.S. Patent No. 4,332,769
2. APHA Standard Methods, 20th ed., p. 4-31, method 4500-CO_2 C (1998)
3. ASTM D 513 - 82, Total and Dissolved Carbon Dioxide In Water, Test Method E

Safety Information

Read MSDS before performing this test procedure. Wear safety glasses.

Reorder Information	**Cat. No.**
***Test Kit**, complete*	*K-1910*

CHEMetrics, Inc., 4295 Catlett Road, Calverton, VA 20138-0214 U.S.A.
Phone: (800) 356-3072; Fax: (540) 788-4856; E-Mail: orders@chemetrics.com

1521-7

Total Alkalinity Titrets® 10 - 100 ppm

Test Procedure

1. Fill the sample cup to the 20 mL mark with your sample (fig. 1).
2. Add 6 drops of A-9800 Activator Solution to the sample (fig. 2). Stir briefly to mix the contents of the sample cup.
   NOTE: The sample should now be green. If it is pink, total alkalinity is 0 ppm. There is no need to continue.
3. Gently snap the tip of the glass ampoule at the white ring nearest the end of the tapered tip (fig. 3).
   NOTE: When the tip is snapped, the flexible tubing will remain in place on the tapered neck of the ampoule.
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   NOTE: The rigid sample pipe will extend approximately 1.5 inches beyond the body of the Titrettor.
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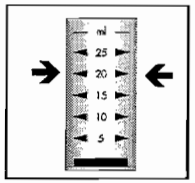


Figure 1

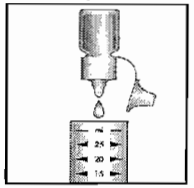


Figure 2

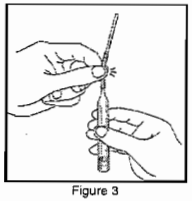


Figure 3

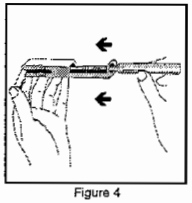
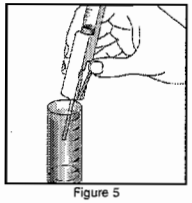


Figure 4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8. Repeat steps 6 and 7 until a permanent color change occurs.

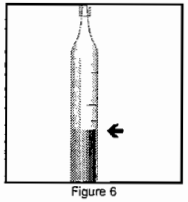
Figure 6

9. When the color of the liquid in the ampoule changes to **GREEN**, remove the ampoule from the Titrettor. Hold the ampoule in a vertical position and read the scale opposite the liquid level (fig. 6). Results are expressed in ppm (mg/Liter) calcium carbonate ($CaCO_3$).

Test Method

The Total Alkalinity Titrets®[1] test method employs an acid titrant and a mixed pH indicator.[2,3,4] Results are expressed as calcium carbonate ($CaCO_3$).

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3. APHA Standard Methods, 20th ed., p. 2-27, method 2320 B (1998)
4. EPA Methods for Chemical Analysis of Water and Wastes, method 310.1 (1983)

Safety Information

Read MSDS before performing this test procedure. Wear safety glasses.

Reorder Information	**Cat. No.**
Test Kit, complete	*K-9810*

Kits are available for total alkalinity analysis at other levels.

CHEMetrics, Inc., 4295 Catlett Road, Calverton, VA 20138-0214 U.S.A.
Phone: (800) 356-3072; Fax: (540) 788-4856; E-Mail: orders@chemetrics.com

0492-7

Carbon Dioxide Titrets®
10 - 100 ppm

Test Procedure

1. Fill the sample cup to the 20 mL mark with your sample (fig. 1).
2. Add 2 drops of A-1900 Activator Solution to the sample (fig. 2). Stir briefly to mix the contents of the sample cup.

   NOTE: If the sample turns pink, carbon dioxide is 0 ppm. There is no need to continue.
3. Gently snap the tip of the glass ampoule at the white ring nearest the end of the tapered tip (fig. 3).

   NOTE: When the tip is snapped, the flexible tubing will remain in place on the tapered neck of the ampoule.
4. Lift the control bar and insert the Titret assembly into the Titrettor (fig. 4).

   NOTE: The rigid sample pipe will extend approximately 1.5 inches beyond the body of the Titrettor.
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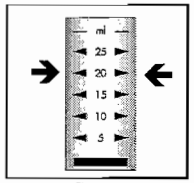


Figure 1

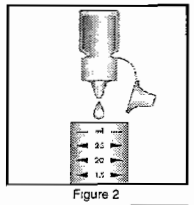


Figure 2

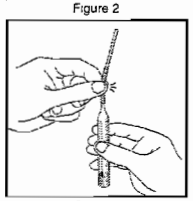


Figure 3

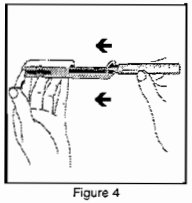
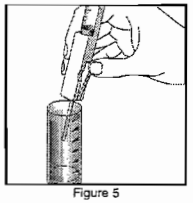


Figure 4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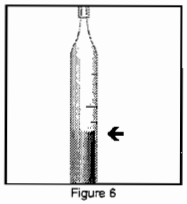
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Test Method

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mL of A-1905 Solution = ppm sulfide ÷ 10

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2. APHA Standard Methods, 20th ed., p. 4-31, method 4500-CO_2 C (1998)
3. ASTM D 513 - 82, Total and Dissolved Carbon Dioxide In Water, Test Method E

Safety Information

Read MSDS before performing this test procedure. Wear safety glasses.

Reorder Information	**Cat. No.**
***Test Kit**, complete*	*K-1910*

CHEMetrics, Inc., 4295 Catlett Road, Calverton, VA 20138-0214 U.S.A.
Phone: (800) 356-3072; Fax: (540) 788-4856; E-Mail: orders@chemetrics.com

Alkalinity (total)

References: ASTM D 1067-92, Acidity or Alkalinity of Water.
APHA Standard Methods, 19th ed., p. 2-26, method 2320B (1995).
EPA Methods for Chemical Analysis of Water and Wastes, method 310.1 (1983).

The alkalinity of water is a measurement of its buffering capacity or ability to react with strong acids to a designated pH. Alkalinity of natural waters is typically a combination of bicarbonate, carbonate and hydroxide ions. Sewage and wastewaters usually exhibit higher alkalinities either due to the presence of silicates and phosphates or to a concentration of the ions from natural waters.

Alkalinity inhibits corrosion in boiler and cooling waters and is therefore a desired quality which must be maintained. It is also measured as a means of controlling water and wastewater treatment processes or the quality of various process waters. In natural waters, excessive alkalinity can render water unsuitable for irrigation purposes and may indicate the presence of industrial effluents.

The Titrimetric Method. CHEMetrics' tests determine total or "M" alkalinity using an acid titrant and a pH indicator. The end point of the titration occurs at pH 4.5. Results are expressed as ppm (mg/L) $CaCO_3$.

Analyte: ALKALINITY (total)
Method: HYDROCHLORIC ACID TITRANT WITH A pH INDICATOR
Type: Titret

Range PPM	MDL PPM	Kit Cat. No.	Price, $	Refill Cat.No.	Refill Price
10-100	10	K-9810	28.00	N/A	N/A
50-500	50	K-9815	28.00	N/A	N/A
100-1000	100	K-9820	26.90	N/A	N/A

The Atlas S-11 July, 2006 data had ranges between 15 and 60 mg/L total alkalinity. EPA/600/R-98/128 Table 2.2 requires a minimum quantification limit of 50 mg/L with a standard deviation of +-20 mg/L. Therefore, use K-9810. Analyze sample within one hour of collection.

Carbon dioxide (dissolved)

References: APHA Standard Methods, 19th ed., p. 4-17, method 4500-CO2 C (1995).
ASTM D 513-82, Total and Dissolved Carbon Dioxide in Water, Test Method E.

Dissolved carbon dioxide (CO2) is present naturally as a result of animal respiration, the decay of organic matter, and the decomposition of certain minerals. It is the major source of acidity in unpolluted water samples. Surface waters typically contain less than 10 ppm (mg/L) dissolved CO2, while ground waters, particularly if deep, may contain several hundred ppm (mg/L). Oil production brines also contain high CO2 concentrations.

High levels of CO2 in surface waters can indicate abnormal organic or mineral decomposition. Measurement of CO2 is a means for monitoring the quality of municipal water treatment systems. Dissolved CO2 is corrosive to water handling equipment, particularly steam condensate systems. Some CO2 is desirable as it helps maintain the carbonate equilibrium, thus avoiding the formation of calcite scale on exposed surfaces. Due to the delicate balance between corrosion and scale formation, CO2 concentrations must be carefully monitored.

The Titrimetric Method. CHEMetrics' carbon dioxide test kits employ a caustic titrant and phenolphthalein indicator. The kits contain a neutralizer solution to correct for sulfide interference.

Analyte: CARBON DIOXIDE (dissolved)
Method: SODIUM HYDROXIDE TITRANT WITH A pH INDICATOR.
Type: Titret

Range PPM	MDL PPM	Kit Cat. No.	Price, $	Refill Cat.No.	Refill Price
10-100	10	K-1910	28.00	N/A	N/A
100-1000	100	K-1920	28.00	N/A	N/A
250-2500	250	K-1925	26.90	N/A	N/A

Titrets® simplify titration tests just as CHEMets® and Vacu-vials® simplify colorimetric tests.

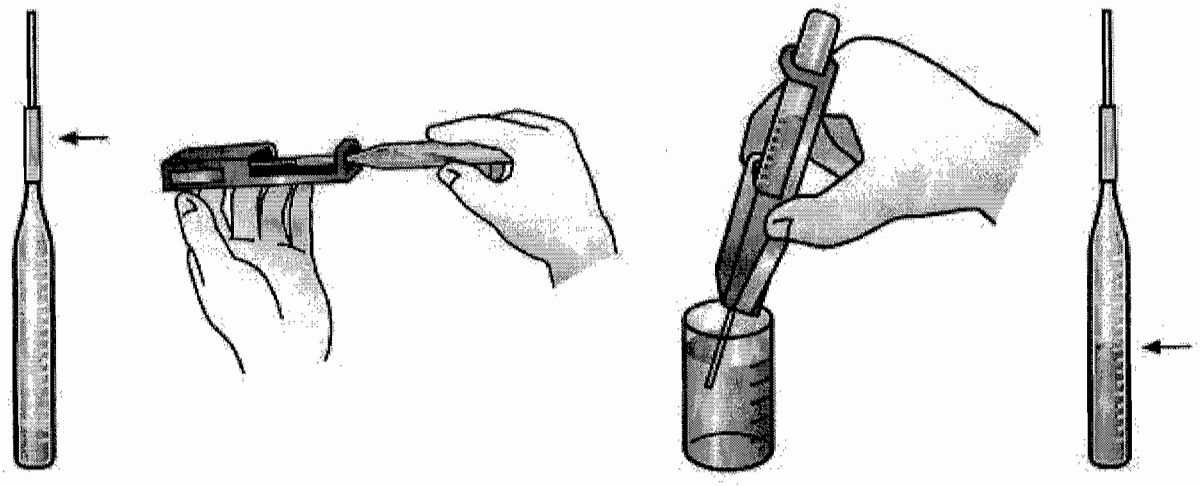
How to use **Titrets®**

Each Titret™ contains a carefully measured quantity of titrant sealed under vacuum. The sealed tip is fitted with a miniature valve that is used to control the flow of sample ***into*** the ampoule as the analyst performs what is known as a "reverse titration."

Sample is drawn into the ampoule in small increments (with mixing) while the analyst watches for the **color change** which signals the end-point of the titration. When that change occurs, the ampoule is placed in an upright position and **the test result is read opposite the location of the liquid level, using a scale printed on the side of the tube.**

The entire process requires only a minute or two and avoids all the equipment hassle and clean-up associated with ordinary titrations.

HOW TO USE Titrets®

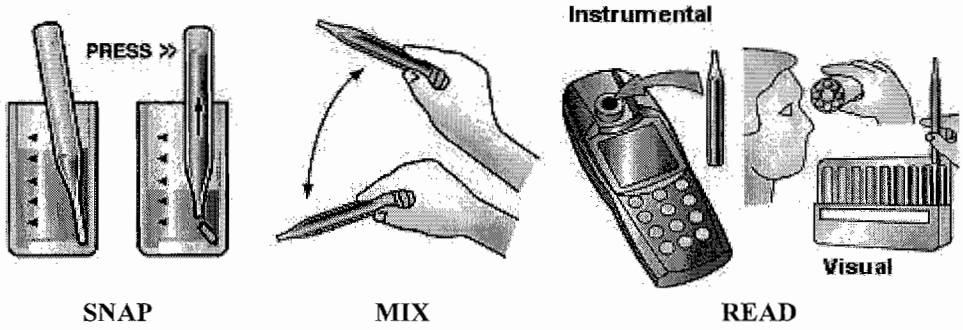


ATTACH VALVE **INSERT Titret into Titrettor™** **TITRATE** **READ**

Since 1969, when CHEMetrics introduced the concept, the self-filling reagent ampoule has been simplifying water testing for analysts all over the world. The key elements of colorimetric analysis -- reagent formulation, measurement and dispensing of the reagent, and measurement of the sample -- are all embodied in this unique, safe, dependable package.

The exact quantity of pre-formulated reagent needed for a single test is ***sealed***

under vacuum in the tapered tip ampoule. The tip is scored for dependable fracture *when you're ready* to perform an analysis. Simply snap the tip of the ampoule in the sample. ***It will fill instantly*** as sample flows into the tube and mixes with the color-forming reagent inside. You can choose visual or instrumental methods to quantify your result.



How can self-filling ampoules save me $$$?

When the cost of performing a test is calculated, whether it's in the lab or out in the field, the key element is ***time*** - - the time it takes to get ready, the time it takes to do the actual test, and finally, the time it takes to clean up. In all of these areas, CHEMetrics' ampoules save dollars, because time-consuming chores have been eliminated by the features we build into each ampoule. We formulate the **reagent *in liquid form*** with buffers and anti-interference components and **we measure the dosage** for you. **We also measure the sample** for you and then, after the test is done, **we let you walk away without glassware to clean up**. All these features save you time, and *that's money*! Compare the ordinary test kit procedures, with their slow-dissolving tablets or powdered reagents put up in "fumble packs," to the CHEMetrics way. It will be clear that our self-filling ampoules mean savings.

What about safety?

Some reagents have hazardous properties - - that's unavoidable. But when you use self-filling ampoules, contact and exposure are minimized because the ***reagent packaged in the ampoule remains in the ampoule***, even after testing is finished. That means that CHEMetrics' tests are safer to use than ordinary methods that require the analyst to handle and dispense potentially dangerous chemicals. (N.B. Caution is advised when performing any chemical operation. Some self-filling ampoule tests require the use of accessory reagents which must be added directly to the sample. Disposal of all chemical materials is subject to governmental regulation.)

Colorimetric test ampoules for visual and photometric readout.

The exact quantity of pre-formulated reagent needed for a single test is sealed under vacuum in the tapered tip ampoule. The tip is scored for dependable fracture *when you're ready* to perform an analysis. Simply snap the tip of the

ampoule in the sample. ***It will fill instantly*** as sample flows into the tube and mixes with the color-forming reagent inside. You can choose visual or instrumental methods to quantify your result. The basic, snap-mix-read simplicity of the self-filling ampoule concept is available in four versions: **CHEMets®**, **Vacu-vials®**, **ULR CHEMets®** and **TRACE Vacu-vials®**.

Auto-diluting ampoules for high range analysis.

VACUettes® are CHEMetrics' answer to another of the analyst's headaches - - diluting samples so that they fall within the applicable range of a colorimetric method. Each Vacuette ampoule is a CHEMet that's fitted with a pre-calibrated capillary pipette at the tip. When high concentrations of analyte are to be measured, the capillary automatically captures the proper volume of sample. The analyst then simply snaps the tip of the ampoule in *dilution water* to flush the contents of the capillary into the tube, diluting it at the same time. Capillaries of various sizes are used to provide a variety of dilution ratios. (See also **VACUettes®**)

Titration tests with self-filling ampoules.

Titrets® simplify titration tests just as CHEMets and Vacu-vials simplify colorimetric tests. Each Titret contains a carefully measured quantity of titrant sealed under vacuum. The sealed tip of the ampoule is fitted with a miniature valve that is used to control the flow of sample ***into*** the ampoule as the analyst performs what is known as a **"reverse titration."** Sample is introduced into the ampoule in small increments (with mixing) while the analyst watches for the color change which signals the end-point of the titration. When that change occurs, the ampoule is placed in an upright position and the test result is read opposite the location of the liquid level, using a scale printed on the side of the tube. The entire process requires only a minute or two and avoids all the equipment hassle and clean-up associated with ordinary titrations. (See also Titrets.)

1-800-356-3072

CHEMets® ampoules are designed for maximum simplicity and accuracy. Use them for low- to medium-range colorimetric analysis. Each ampoule is 7 mm in diameter with a tapered, prescored tip. Reagents are vacuum sealed inside.

The CHEMets® Method: The analyst immerses the CHEMet ampoule in the sample and snaps the tip. The correct volume of sample is drawn in by vacuum, and a small inert gas bubble remains. Sample and reagent are mixed by tilting the ampoule so the bubble travels from end to end. In 2 minutes or less, the resulting color is compared to the appropriate color standards to quantify the result.

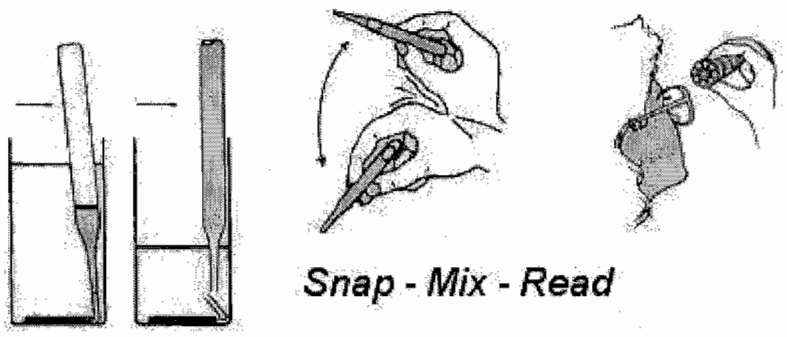
Low Concentrations (Less than 1 ppm.) In most cases the cylindrical comparator is used to quantify low concentrations. The filled test ampoule is placed in the center and compared with the eight color standards surrounding it.

Medium Concentrations (Above 1 ppm.) The flat comparator is usually used for concentrations higher than 1 ppm. The analyst places the filled ampoule next to individual standards until a color match is found.

Each ULR ampoule is 8 mm in diameter and 250 mm in length with a tapered, prescored tip. Reagents are vacuum sealed inside.

The ULR CHEMets® Method.
The ULR CHEMet™ ampoule is immersed in the sample and the tip is snapped off. The correct volume of sample is drawn in, and a small inert gas bubble forms. Sample and reagent are mixed by tilting the ampoule so that the bubble travels from end to end. In 2 minutes or less, the resulting color is compared to the appropriate color standards to quantify the result.

ULR CHEMets® enable the user to **measure concentrations at very low levels**. A cylindrical comparator is used to read the test results. The filled test ampoule is placed in the center of the cylinder and compared with eight color standards surrounding it.



Test kits contain 30 ampoules, comparator(s), accessory solutions (when necessary), snap cup, MSDS, and instructions. Refill packs of 30 ampoules, and accessory solutions, are available.

Comparators have a 2-year shelf-life. Material Safety Data Sheets are provided in test kits.

APPENDIX 2

Field Forms from July, 2006 Monitoring Event

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	MW-03	Pump On Time:	1210
Personnel:	CB/ES	Total Depth	136.7ft	Pump Off Time:	1336
Date:	7/27/06	Initial DTW:	22.3ft	Sample Collected Time:	1335
Start PID:	0.0ppm	Final DTW:	21.2ft	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Open		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.25 GPM		
		Sample Method:	Low flow - 2-Inch Grundfos Pump, Horiba U-11, Flow-Through Cell		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1220	22.30	5.97	9.70	10.00	0.206	28	-45	91.70	0.01	2.30	40
1225	21.70	6.17	9.23	10.00	0.205	24	-57	162.00	0.01	2.00	40
1230	21.30	6.19	9.71	10.00	0.206	20	-55	120.00	0.01	2.00	40
1235	21.00	6.19	9.68	10.00	0.203	20	-57	122.00	0.01	2.00	40
1240	21.00	6.15	9.55	10.00	0.206	20	-50	120.00	0.01	2.00	40
1245	21.12	6.18	9.50	10.00	0.206	20	-55	118.00	0.01	2.00	40
1250	21.16	6.17	9.47	10.00	0.206	20	-53	121.00	0.01	2.00	40
1255	21.18	6.20	9.51	10.00	0.209	20	-51	123.00	0.01	2.00	40
1300	21.18	6.19	9.55	10.00	0.210	20	-50	123.00	0.01	2.00	40
1305	21.20	6.17	9.50	10.00	0.209	20	-53	123.00	0.01	2.00	40
1310	21.20										

Additional Information:

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	PW-24	Pump On Time:	1535
Personnel:	CB/ES	Total Depth	Unknown	Pump Off Time:	1605
Date:	7/27/06	Initial DTW:	Unknown	Sample Collected Time:	1555/1600
Start PID:	0.0ppm	Final DTW:	Unknown	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Unknown		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.5 GPM		
		Sample Method:	Natural Spring Outfall Pipe		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1540		7.31	12.30	0.00	0.273	52	342	3.90	0.00	0.00	45
1545		6.51	10.70	9.41	0.220	52	362	3.90	0.00	0.00	45
1550		6.50	10.70	19.22	0.222	52	358	5.30	0.00	0.00	45

Additional Information: Collected Duplicate and MS/MSD

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	PW-35	Pump On Time:	1410
Personnel:	A. Salazar	Total Depth	42ft	Pump Off Time:	1445
Date:	7/27/06	Initial DTW:	Unknown	Sample Collected Time:	1435
Start PID:	0.0ppm	Final DTW:	Unknown	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Unknown		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.5 GPM		
		Sample Method:	Bypass Spigot		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1415		7.07	14.00	0.63	0.880	80	382	0.00	0.00	0.00	15
1425		6.95	12.20	0.70	0.725	80	385	3.60	0.00	0.00	15
1430		6.92	12.60	0.63	0.619	80	379	4.60	0.00	0.00	15

Additional Information: Bypass Spigot in basement

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	PW-68	Pump On Time:	1315
Personnel:	A. Salazar	Total Depth	Unknown	Pump Off Time:	1355
Date:	7/27/06	Initial DTW:	Unknown	Sample Collected Time:	1335
Start PID:	0.0ppm	Final DTW:	Unknown	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Unknown		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.5 GPM		
		Sample Method:	Bypass Spigot		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1325		7.10	22.90	2.52	0.553	74	691	1.00	0.00	0.00	60
1330		7.06	22.80	4.71	0.684	74	704	0.50	0.00	0.00	60
1335		6.92	21.70	2.34	0.667	74	511	0.70	0.00	0.00	60

Additional Information: Bypass Spigot in basement

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	PW-80	Pump On Time:	1225
Personnel:	A. Salazar	Total Depth	90ft	Pump Off Time:	1255
Date:	7/27/06	Initial DTW:	Unknown	Sample Collected Time:	1245
Start PID:	0.0ppm	Final DTW:	Unknown	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Unknown		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.5 GPM		
		Sample Method:	Tap		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1230		6.00	17.00	5.03	0.209	120	187	1.40	0.00	0.00	40
1235		6.21	16.80	5.04	0.208	120	189	4.00	0.00	0.00	40
1240		6.25	16.70	4.99	0.204	120	199	1.60	0.00	0.00	40

Additional Information: Tap in kitchen

Sampling Log Form
Atlas Site S-11
Ellendburg, New York

Site ID:	Atlas S-11	Well Number:	PW-118	Pump On Time:	1700
Personnel:	CB/ES	Total Depth	Unknown	Pump Off Time:	1730
Date:	7/27/06	Initial DTW:	Unknown	Sample Collected Time:	1720
Start PID:	0.0ppm	Final DTW:	Unknown	Sample Analysis:	VOC; methane/ethane/ethene; sulfide; sulfate
End PID:	0.0ppm	Screened Interval:	Unknown		HACH - CO2, Alkalinity, Fe2+
		Purge Rate:	0.5 GPM		
		Sample Method:	Bypass Spigot		

Time (3 - 5mins)	**DTW** (0.3ft)	**pH** (0.1 Units)	**Temp** (°C)	**DO** (g/L) (10%)	**Cond.** (ms/m) (3%)	**CO_2** (mg/L)	**ORP** (mV)	**Turbidity** (NTU) (10%)	**Salinity**	**Iron (Fe^{+2})**	**Alkalinity**
1700		6.77	26.00	4.57	0.459	100	30	11.8	0.02	0.00	25
1705		6.73	18.18	3.31	0.502	100	35	36	0.02	0.00	25
1710		6.78	19.81	9.08	0.498	100	41	0.6	0.02	0.00	25
1715		6.85	17.84	9.08	0.513	100	145	20	0.02	0.00	25

Additional Information:

APPENDIX 3

Laboratory Standard Operating Procedures and Quality Control Requirements

Note: The laboratory SOPs are uncontrolled copies, so they cannot be printed out in a legible fashion. Adobe Acrobat PDF files are provided on the attached CD for the following methods:

376.1 sulfide

353.2 nitrate nitrogen

RSK-175 dissolved gases in groundwater

524.2 VOCs in potable water

350.2 ammonia nitrogen

365.2 total phosphorous

300.0 inorganic ions by ion chromatography

SOP No.	Revision No.	Date	Page
UWC-376.1	11	03/16/07	1 of 27

TITLE: WET CHEMISTRY
Total Acid Soluble, Acid-Volatile, and Reactive Sulfide

Updated by:	Signature:	Date:
Carla Bonner Supervisor, Wet Chemistry	Carla Bonner	3/12/07

Approved by:	Signature:	Date:
Diane L. Harper Inorganics Manager	Diane L. Harper	3-12-07
David W. Mazur Env. Health & Safety Coor.	D. W. Mazur	3/13/07
Terese A. Preston Quality Manager	Terese A. Preston	3/14/07

CONTROLLED DISTRIBUTION

COPY # :

ISSUED TO : **Uncontrolled**

Full Signature Approvals Are Kept on File
With STL's QA Standard Practice Records

1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) describes the procedure to determine the concentration of sulfides in drinking, surface and saline waters and of acid soluble and reactive sulfides in solid wastes and soils. This SOP was written using the following references:

- SW-846, 3rd Edition, Method 9030B (distillation) and 9034 (titration) (for acid extractable analysis).
- Standard Methods, 20th Ed., Method 4500-S^{2-}F or E, 4500-S^{2-}C (for waters). There may be several references to the equivalent EPA Method 376.1 throughout this SOP. As of March 12, 2007, this method has been withdrawn from the Federal Register. There will be a transition period in which the method is removed from laboratory, agency and permit documentation. Regardless, STL Chicago will remain in compliance with approved methods and regulations.
- SW-846, 3rd Edition, Section 7.3.4.2 for Reactive Sulfide in solid waste. This method has been withdrawn by the US EPA, but it is frequently requested by STL Clients and therefore kept in this SOP.
- Draft Analytical Method for Determination of Acid Volatile Sulfide in Sediment, USEPA, 1991 (E 821/R-91-100)

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are set

higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	1 mg/L
Soils/Waste	25 mg/kg
Reactive solids	50 mg/kg
Acid Volatile Sulfide (AVS)	25 mg/Kg

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

For acid-soluble sulfide, reactive sulfide, or acid-volatile sulfide (AVS) samples, separation of sulfide from the sample matrix is accomplished by the addition of acid to the sample in a closed system in which the hydrogen sulfide (H_2S) formed is carried by a nitrogen stream into a zinc acetate gas scrubbing bottle, where it is precipitated as zinc sulfide.

The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of iodine, in excess of that required by the sample. Then the excess iodine is determined by titration with a standard solution of sodium thiosulfate until the blue iodine starch complex disappears. Quantitation is based on the volume of sodium thiosulfate required.

Water samples may be treated for interferences or concentrated by precipitation, filtration, and re-suspension, or may be titrated directly.

This method provides only a semi-quantitative determination of sulfide compounds considered "acid-insoluble" (i.e., CuS; SnS_2) in solid samples.

Note: The US EPA has determined that the method for reactive sulfide is unreliable, and recommends that laboratories analyze samples for total sulfide instead. This is the practice at STL Chicago for any water samples that are received for reactive sulfide. However, STL Chicago does follow SW 846 Section 7.3.4.2 for reactive sulfide in soils and wastes.

2.0 INTERFERENCES

- Prior to preservation and precipitation of the sulfide in water samples by zinc acetate, the sample should not be agitated.

- The iodometric method suffers interferences from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds, both solid and dissolved.
- Eliminate interferences due to sulfite, thiosulfate, iodide and many other soluble substances (not including ferrocyanide) by first precipitating zinc sulfide, then removing the supernatant and replacing with deionized water.
- Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid and may form sulfur dioxide. This could create a positive interference and false high values.
- SW-846 states that adding formaldehyde to the scrubber solution can eliminate this interference but due to employee safety considerations, STL Chicago does not use formaldehyde.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

Sodium Sulfide will form Hydrogen Sulfide (H_2S) gas if combined with water moisture or strong acids. Inhalation of H_2S gas can cause headache, dizziness, nausea, and unconsciousness and potentially death.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (H_2S) gas if combined with strong acids. Inhalation of gas (H_2S) may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Sulfuric Acid	Corrosive Oxidizer Dehydra-dator	1 mg/m^3	This material will cause burns if comes into contact with the skin or eyes. Inhalation of vapors will cause irritation of the nasal and respiratory system.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

- Westco Easy-dist jr. sulfide glassware
- 20-place block digester
- 5 mL volumetric pipets
- 10 mL disposable pipettes
- Top-loading balance
- Digital buret
- Nitrogen gas
- Glass fiber filters
- Extension funnel

5.0 REAGENTS AND STANDARDS

All reagents are prepared with Type II Deionized Water, unless otherwise specified, in class A volumetric flask. Use reagent grade chemicals.

5.1 Iodine Solution, ~0.025 N

Dissolve 20 to 25 grams potassium iodide in ~500 mL DI water in a 1.0 L Class A volumetric flask. Add 3.2 grams iodine. After the iodine has dissolved, dilute to volume and standardize daily against standard sodium thiosulfate using starch indicator.

- Life of Reagent: 1 year
- Storage Requirements: Store in dark bottle 15 - 30°C.

5.2 Hydrochloric Acid, Concentrated

Purchased from a chemical vendor.

- Life of Reagent: 5 years
- Storage Requirements: none

5.3 6 N Hydrochloric Acid

Slowly add 500 mL of concentrated hydrochloric acid to a 1.0 L volumetric flask containing ~450 mL DI water. Cool and dilute to volume with DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.4 Sodium Thiosulfate, ~0.025 N

Using an analytical balance capable of measuring 0.1 mg, weigh out 6.205 grams sodium thiosulfate [$Na_2S_2O_3 \cdot 5H_2O$] and quantitatively transfer to a 1.0 L Class A volumetric flask. Add 1.5 mL 6 N sodium hydroxide (NaOH) or 0.4 grams solid sodium hydroxide and dilute to just under 1.0 L with DI water. Standardize upon preparation with potassium bi-iodate solution as follows:

Dissolve 2 grams potassium iodide in an Erlenmeyer flask with 150 mL DI water. Add a few drops of concentrated sulfuric acid and 10.0 mLs of Standard Potassium Bi-iodate solution using a volumetric pipette. Dilute to ~200 mL. Titrate with Standard Sodium Thiosulfate until a pale straw color is reached. Add starch indicator and continue titrating to the first disappearance of the blue color. Determine the Normality of the Sodium Thiosulfate using the following calculation:

(N) (V) = (0.025 N) (10.0 mLs)

Where:
N = Normality of Sodium Thiosulfate
V = volume of Sodium Thiosulfate
Standardize in triplicate and use the average value in calculating the Normality.

- Life of Reagent: 1 year
- Storage Requirements: none

5.5 Starch Indicator

Dissolve 2 g laboratory grade soluble starch and 0.2 g Salicylic Acid, as a preservative, in 100 mLs hot DI water. Alternatively, this can be purchased from a vendor or a powdered starch form can be used.

- Life of Reagent: 1 year
- Storage Requirements: refrigerate

5.6 0.5 M Zinc Acetate

Dissolve 110 g Zinc acetate dihydrate in 200 mL of reagent water. Add 1 mL of concentrated HCl to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

- Life of Reagent: 1 year
- Storage Requirements: none

5.7 Sulfide Stock 1, ~200 mg/L W S T S F 1 _ _

Dissolve 1.500 grams of sodium sulfide [$Na_2S \cdot 9H_20$] in a 1.0 L Class A volumetric flask with DI water. Add 5 mL of 2 N Zinc Acetate solution as a preservative. The "true value" is determined upon preparation by averaging the titration results of 3 aliquots. Using a 5.0 mL volumetric pipette, add 5.0 mL of well-mixed Stock Sulfide Solution to ~100 mLs and titrate as for a sample (See section 7). Calculate the sulfide concentration using 5 mL as the sample volume. Repeat 2 times and average the concentrations for use as the "true value".

- Life of Reagent: 1 year
- Storage Requirements: store in amber bottle

5.8 0.25 N Sodium Hydroxide

Dissolve 10 grams of sodium hydroxide pellets in 1000 mL of DI water in a volumetric flask. This reagent is used for both the Cyanide and Sulfide tests.

- Life of Reagent: 1 year
- Storage Requirements: none

5.9 Potassium bi-iodate, 0.0021 M

Using an analytical balance capable of measuring 0.1 mg, quantitatively transfer 0.8124 g potassium bi-iodate to a 1.0 L volumetric flask using DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.10 Sodium Hydroxide, 6 N

Dissolve 240 g of sodium hydroxide into 1.0 liter of DI water.

- Life of Reagent: 1 year
- Storage Requirements: none

5.11 0.1 N Sulfuric Acid

Dilute 2.8 mLs concentrated H_2SO_4 to 1.0 L to make the 0.1 N H_2SO_4. This reagent is used for both reactive cyanide and reactive sulfide.

- Life of Reagent: 1 year
- Storage Requirements: none

5.12 2 N Zinc Acetate

Dissolve 220 g Zinc Acetate Monohydrate [$Zn(C_2H_3O_2)_2 \cdot H_2O$] in ~850 mL of DI water in a 1.0 L volumetric flask. Dilute to volume with DI water.

- Life of Reagent: 1 - year
- Storage Requirements: none

5.13 20 % Sulfuric Acid

To a 1.0 L volumetric flask containing ~600 mLs DI water, slowly add 200 mLs of concentrated sulfuric acid. Mix thoroughly. When cool, dilute to volume with DI water.

- Life of Reagent: 1 - year
- Storage Requirements: none

5.14 Mercury and ICAP spiking solutions

The spiking solution is obtained from the mercury and metals digestion analysts. The Mercury spiking solution concentration is 100 ug/L.

Life of Reagent: 1 day
Storage Requirements: none

5.15 Aluminum Chloride solution

Dissolve the contents of a previously unopened 100-gram bottle of $AlCl_3 \cdot 6H_2O$ in 100 mL of DI water.

Life of Reagent: 1 year
Storage Requirements: none

6.0 CALIBRATION (NON-DAILY)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

The following Quality Control standards are inherent in each analytical batch.

Quality Controls	Frequency	Control Limit
Iodine Standardization	Prior to Analysis	
Method Blank (MB)	1 in 20 samples[4]	< Reporting Limit
Laboratory Control Sample (LCS) [1]	1 in 20 samples[4]	80 – 120%
Matrix Spike/Matrix Spike Duplicate (MS/MSD) [2,3]	1 in 20 samples[4]	75 - 125%; ≤ 20 RPD

NOTE: The recoveries for Reactive Sulfide are typically low and the in-house statistical limits are used for reporting. SW-846 Section 7.3.4.2 states that a 50% recovery is an indication that the scrubbing system is working adequately.

[1] LCS Duplicate (LCD) is done only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[2] The sample selection for MS/MSD is rotated among client samples so that various matrix problems may be noted and/or addressed.
[3] Matrix Duplicate (MD) is done only when requested by the client/project/contract. The MS/MSD are done routinely.
[4] Acid Volatile Sulfide (AVS) must be analyzed in sets of 10 or fewer samples unless specified otherwise in a project.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times and the references, which includes container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Reference
CWA	7 days	40 CFR Part 136.3

7.3 Sample Preparation

7.3.1 Sample Size

Matrix	Sample Size
Waters	250 mLs
Soils / Wastes	10 grams

7.3.2 Sample Preparation - General

7.3.2.1 If the sample contains solid objects that cannot be reduced in size by tumbling, the solids must be broken manually. The solids must be reduced to a size that will be suspended by the bubbling action of the Westco system.

7.3.2.2 Non-porous harder objects, for example stones or pieces of metal, may be weighed and discarded. This is done by removing rocks, etc., from the sample after the initial weighing.

7.3.3 Sample Preparation - Waters for Total Sulfide (EPA Method 376.1 and Std. Mds., 20th Ed., Method 4500S^{-2}B and C

7.3.3.1 If a water sample is received unpreserved, add 0.75 mL (15 drops) 2 N zinc acetate solution to a 500 mL bottle. With minimal agitation, fill with sample. Add 0.50 mL (10 drops) 6 N sodium hydroxide solution. Alternatively, add one zinc acetate-sodium hydroxide preservative ampule to 1 L of sample. Mix well by rotating the bottle back and forth about a transverse axis. Let the precipitate settle for 30 minutes. The treated sample is relatively stable. However, if much iron is present, oxidation may occur.

7.3.3.2 If a sample is known to contain interferences, the preserved sample may be de-watered by filtering a known volume through a glass fiber filter (Reference Method 4500S^{-2}C). The zinc sulfide precipitate is captured on the filter, and the filtrate that

contains interferences is discarded. This procedure may also be used to concentrate larger volumes of sample to achieve a lower reporting limit. Specifically see Section 7.6.2 for de-watered samples.

7.3.3.4. If dissolved sulfide is required, add 1.0 mL of 6 N NaOH to a 500 mL bottle. Fill the bottle with sample and add 1.0 mL of aluminum chloride reagent. Close the bottle, eliminating air entrapment. Mix very well for one minute to flocculate the contents. Allow to settle until reasonably clear, but do not wait longer than necessary. Draw off 250 mL of the cleared supernate for analysis.

Proceed to Section 7.6.

7.3.4 Sample Preparation - Waste Samples for Total Sulfide (SW-846 Method 9030B)

7.3.4.1 Weigh 10 grams of well-mixed sample to the nearest 0.1 gram, into a tared Westco boiling tube, or weigh the sample portion onto a tared piece of parafilm or weigh boat and transfer into a Westco tube. Record the sample weight in the > weigh log.

7.3.4.2 Add 50 mL of DI water to each sample, the MS and MSD, and to separate tubes for the MB and LCS.

7.3.4.3 Add 10.0 mL of well-mixed stock sulfide to the LCS, MS, and MSD. This is best accomplished by setting the stock solution on a stir plate, adding a stir bar, and mixing at a steady rate. While mixing, withdraw the 10.0 mL using a 10.0-mL volumetric pipet. The sulfide is contained in the suspended precipitate of the standard.

7.3.4.4 Place the inlet adapter tube into the prepared boiling tubes and place into the block digester.

7.3.4.5 Close the stopcock of the Westco addition funnels and add 50 mL of 20% sulfuric acid to the funnel. This volume of acid will neutralize and pH adjust 10 g NaOH, thereby ensuring that any 10-gram sample will be adequately acidified. Cap the addition funnels and set them on top of the inlet tubes.

7.3.4.6 Add 50 mL of 0.25 N NaOH and 5 mL of 0.5 N zinc acetate to 2 Westco scrubbing vessels for each sample/standard.

7.3.4.7 Connect all the glassware and gas tubing, ensuring tight fits.

7.3.4.8 Open the N_2 gas regulator slightly, and adjust the system so that the gas is bubbling through all the glassware. The gas flow not only sweeps the sulfide gas into the scrubbers, it also "stirs" the samples during the extraction.

7.3.4.9 Allow to purge for approximately 10 minutes to remove the oxygen from the system. Make sure that each tube is bubbling. Some samples tend to block the

inlet tube, and may require lifting the tube from the bottom of the sample while the gas is flowing to release a plug, or increasing the gas flow, or both.

7.3.4.10 Turn on the heating block, after programming it for sulfide. (The block ramps at a rate of 8 degs. per minute to 70 degs., and holds that temperature for 1.5 hrs.)

7.3.4.11 Open the addition funnel stopcocks gently, watching for excess reactivity. When all the acid is dispensed, re-close the stopcocks and allow the reaction to occur for 90 minutes, checking the gas flow frequently.

7.3.4.12 After 90 minutes, turn off the gas and disassemble the apparatus. The contents of both scrubbers are combined and titrated.

7.3.4.13 Proceed to Step 7.6.

7.3.5 Sample Preparation - Waste Samples for Reactive Sulfide SW-846, Section 7.3.4.2

7.3.5.1 Weigh 10 grams of sample to the nearest 0.1 gram, into a tared Westco boiling tube, or weigh the sample portion onto a tared piece of parafilm or weigh boat and transfer into a Westco tube. Record the sample weight in the weigh log.

7.3.5.2 Add 100 mL of DI water to each sample, the MS and MSD, and to separate tubes for the MB and LCS.

7.3.5.3 Add 10.0 mL of well-mixed stock sulfide to the LCS, MS, and MSD. This is best accomplished by setting the stock solution on a stir plate, adding a stir bar, and mixing at a steady rate. While mixing, withdraw the 10.0 mL using a 10.0-mL volumetric pipet. The sulfide is contained in the suspended precipitate of the standard.

7.3.5.4 Place the inlet adapter tube into the prepared boiling tubes and place into the block digester.

7.3.5.5 Close the stopcock of the Westco addition funnels and add 11 mL of 0.1 N sulfuric acid to the funnel. This amount added to the 100 mL in the boiling tube will be equivalent to 0.01N sulfuric as required by SW 846. Set the addition funnels on top of the inlet adapters.

7.3.5.6 Add 50 mL of 0.25 N NaOH and 5 mL of 0.5 N zinc acetate to one Westco scrubbing vessels for each sample/standard. Assemble all the Westco glassware and gas tubes.

7.3.5.7 Turn on the N_2 gas with the regulator on the lowest mark. Check for consistent bubbling throughout the system, and allow the system to purge for approximately 10 minutes. (See 7.3.4.10)

7.3.5.8 Open the stopcock to allow the acid in the addition funnel to boiling tube with sample. Allow the reaction to proceed for 30 minutes, then disassemble the apparatus. The sulfide trapped in the scrubber is now ready for analysis.

7.3.5.9 Proceed to Section 7.6.

7.3.6 Sample Preparation - Water Samples for Reactive Sulfide SW-846, Section 7.3.4.2

Same as the waste procedure (Section 7.3.5) except the sample size is 100 mLs rather than 10 grams. This procedure is rarely done. Generally, reactive sulfide in waters is done as total sulfide.

7.3.7 Sample Preparation – Sediments for Acid Volatile Sulfide

7.3.7.1 De-oxygenate ~ 500 mL of 6N HCl (reagent 5.3) by bubbling nitrogen gas through the solution for ~ 1 hour.

7.3.7.2 Weigh ~10 grams of sample onto a ~2" square of Parafilm. Roll sufficiently to fit into the Westco sample tubes. Alternatively, drier samples can be weighed directly into the tared sample tubes. Record the sample weight in the weigh log.

7.3.7.3 Add 100 mL of DI water to each tube. Disperse any sample that may be caught in the weighing Parafilm, then temporarily cover the tubes with Parafilm.

7.3.7.4 Add 10.0 mL of well-mixed stock sulfide to the LCS tube and duplicate portions of at least one sample per 10. Withdraw the sulfide stock while the stock is being stirred on a stir plate. Add 2.5 mL of ICAP spiking solution (obtained from metals digestion group) and 2.5 mL of a 100 mg/L mercury spiking solution (obtained from the mercury analyst) to a separate LCS and separate duplicate portions of at least one sample in 10. *Note: mixing the metals and sulfide spikes will likely result in low recoveries for each.*

7.3.7.5 Add 5 mL of 0.5M zinc acetate (reagent 5.6), and 50 mL of 0.25 N NaOH (reagent 5.8) to the scrubber pair for each sample/standard. The metals LCS and MS/MSD do not need scrubbers.

7.3.7.6 Assemble Westco sulfide glassware in supportive rack, connecting nitrogen gas tubing to manifold and from the manifold to the two gas inlets on the glassware. Secure all the joints, with Parafilm if necessary.

7.3.7.7 Add 20 mL de-oxygenated 6 N HCl to each addition funnel. Make sure the stopcock is closed before you add the acid.

7.3.7.8 Turn on the nitrogen gas and purge for 10 minutes at a low flow rate to de-oxygenate entire system. The stopcock remains closed during purging.

7.3.7.9 Open the stopcocks to add the HCl to the samples. Reduce the flow, but ensure that the gas is bubbling throughout the system by adjusting the connections, flow, etc.

7.3.7.10 Allow the reaction to proceed for 1 hour.

7.3.7.11 Analyze the contents of the scrubbers. See Section 7.

7.3.7.12 Transfer the contents of the Westco sample tubes to 125 mL snap-cap vials and give them to the metals digestion group. There they will be filtered and brought to 250 mL final volume for metals analysis.

7.4 Calibration and QC Preparation

7.4.1 Standardization of Iodine

NOTE: The iodine is standardized daily prior to each use.

7.4.1.1 Using a volumetric pipette, add 5.0 mLs of iodine reagent to each of three 125 mL Erlenmeyer flasks and dilute to 100 mL with DI water.

7.4.1.2 Add approx. 5 mL 6 N hydrochloric acid (Rgt. 5.3) to each.

7.4.1.3 Back titrate each with Std. Sodium Thiosulfate until the solution becomes pale yellow.

7.4.1.4 Add ~0.5 mL of the 2% Starch Solution or starch powder (the color of the sample solution should turn a dark blue - black; if not, the solution has been titrated too far).

7.4.1.5 Continue titrating each of the three until the solution becomes clear. Record the titrant volumes.

7.4.1.6 Use the average mL of titrant in calculating the normality of iodine.

7.4.2 Method Blank (MB) (Water)

Use 250 mL DI Water.

7.4.3 Laboratory Control Sample (LCS) (Water)

Using a 5.0 mL volumetric pipette, add 5.0 mL of well-mixed Stock Sulfide Solution to 250 mL of DI water measured into a 250 mL volumetric flask. This is best accomplished by withdrawing the 5.0 mL while the stock is mixing on a stir plate.

Concentration: ~4.0 mg/L. The "true value" is determined at the time of preparation of the 200 mg/L stock solution. The reagent factor for LabNet is 50.

7.4.4 Matrix Spike / Matrix Spike Duplicate (MS/MSD) (Water)

Using a 5.0 mL volumetric pipet, add 5.0 mL of well-mixed Stock Sulfide Solution to 250 mLs of sample in a 300-mL flask. Note that the sulfide is contained in the suspended precipitate of the standard. It is best to withdraw the stock solution while the stock is mixing on a stir plate.

Concentration: ~4.0 mg/L (See note in 7.4.3) for a 250 mL sample. If a different sample volume was spiked, the reagent factor must be adjusted by 50 X mL sample / 250.

7.4.5 Soil / Waste Method Blank

For Reactive, Total, and Acid Volatile Sulfide, use 100 mL DI water in the Westco sample tubes and treat as a sample.

7.4.6 Soil / Waste Laboratory Control Sample (Total, Reactive, or AVS)

Using a 10.0 mL volumetric pipette, add 10.0 mL of well-mixed Stock Sulfide Solution to 100 mL of water in the Westco sample tube. Note that the sulfide is contained in the suspended precipitate of the standard.

Concentration: ~200 mg/Kg, assuming 10 grams sample. See note in 7.4.3. There is no reagent factor needed for LabNet.

For AVS-SEM only, using Eppendorfs, add 2.5 mL of ICAP and Hg spiking solutions (provided by the metals section) to 100 mL of DI water in a separate Westco tube.

7.4.7 Soil / Waste Matrix Spike / Matrix Spike Duplicate (Total, Reactive, and AVS)

Using a 10.0 mL volumetric pipette, add 10.0 mL of well-mixed Stock Sulfide Solution to the Westco tube containing ~10 grams of sample. Note that the sulfide is contained in the suspended precipitate of the standard.

Concentration: ~200 mg/kg. The reagent factor for LabNet is 1 X sample weight in grams / 10 grams. For metals concentrations, see the appropriate STL Chicago SOPs.

For AVS-SEM only, using Eppendorfs, add 2.5 mL of ICAP and Hg spiking solutions (provided by the metals section) to separate duplicate sample aliquots.

7.5 Preventive Maintenance

- Wash and rinse all tubing daily of any waste particles left inside. Always shut off the gas valve after daily use.
- Rinse the burette with DI water and titrant prior to each use. Rinse with DI water after each use.
- Periodically rinse the tubing with 10% nitric acid, followed by DI water rinsing.

7.6 Sample Analysis

7.6.1 For SW Method 9030B, Reactive Sulfide, or Acid Volatile Sulfide Preparations:

7.6.1.1 Pipet 5.0 mL of standardized 0.025 N iodine and approximately 20 mL of DI water to a =/>300 mL Erlenmeyer flask, using the water to rinse all traces of iodine into the bottom of the flask.

7.6.1.2 Add 6 N HCl in the following amounts:

Total and AVS (2 scrubbers)	Reactive (only 1 scrubber)
9 mLs HCl	6 mLs HCl

7.6.1.3 Keeping the pipet tip below the surface of the iodine solution, pipet the contents of the gas scrubbers into the flasks. A funnel with tubing attached may be used to dispense the sample below the iodine solution level in the titration flask. If the solution does not retain the yellow color, add more 6 N HCl, then if necessary, additional 5.0 mL increments of 0.025 N iodine until the color remains, recording the total amount of iodine used.

NOTE: When adding additional iodine, the sample may become turbid and the yellow color change may be difficult to perceive. At this point, add ~0.5 mLs of the 2% Starch Indicator (Rgt. 5.5) for a distinct blue color change (this occurs in samples with high sulfide content).

7.6.1.4. Continue titrating until the first complete disappearance of the blue color. Blue tinge will come back after sitting. No additional titration is required.

7.6.2 For Dewatered Sample Preparations

7.6.2.1 Place the filter containing the zinc sulfide precipitate into a suitable flask. Add 5.0 mL of standardized 0.025 N iodine and enough DI water to cover the filter. Then add 6 mL of 6 N HCl and re-suspended precipitate by gently swirling. If the solution does not retain the yellow color, add additional 5.0 mL increments of 0.025 N iodine until the color remains, recording the total amount of iodine used.

NOTE: When adding additional iodine, the sample may become turbid and the yellow color change may be difficult to perceive. At this point, add ~0.5 mLs of the 2% Starch Indicator (Rgt. 5.5) for a distinct blue color change (this occurs in samples with high sulfide content).

7.6.2.2 Back titrate with Std. Sodium Thiosulfate (Rgt. 5.4) until the solution turns a straw color, then add enough Starch Indicator (Rgt. 5.5). The color should be blue - black (if the sample remains straw color or colorless, you have titrated too far).

7.6.2.3 Continue titrating until the first complete disappearance of the blue color. Record the titrant volume used. The blue color may come back after sitting. No additional titration is necessary.

7.6.3 For preserved water samples.

7.6.3.1 Pipet 5.0 mL of standardized 0.025 N iodine and approximately 20 mL of DI water to a =/>300 mL Erlenmeyer flask, using the water to rinse all traces of iodine into the bottom of the flask. Add 3 mL of 6 N HCl.

7.6.3.2 Gently invert and swirl the sample to suspend the zinc sulfide precipitate, then poor the appropriate volume (usually 250 mL) through the extension funnel into the flask, keeping the tip below the iodine level.

7.6.3.3 Back titrate with Std. Sodium Thiosulfate (Rgt. 5.4) until the solution turns a straw color, then add enough Starch Indicator (Rgt. 5.5). The color should be blue - black (if the sample remains straw color or colorless, you have titrated too far).

7.6.3.4 Continue titrating until the first complete disappearance of the blue color. Record the titrant volume used. The blue may return upon sitting. No additional titration is necessary.

7.7 Documentation

7.7.1 Analysis Logbook

The analysis of samples and standards is documented within the instrument run log. The runlog must be completed for each day's analysis. An example of an analysis log page appears in Attachment 1.

7.7.2 Traceability of Standards

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into the laboratory's LIMS and is issued a unique ID# based upon the type and sequential order in which the item was received. Further information entered into the database includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item. Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review form (Refer to Attachment 2). Upon the first 100% review, the review form is initialed and the data is set to 1st Level Review. The checklist then goes to the supervisor or peer reviewer for a second review. Once again, the review form is initialed and dated by the second reviewer who sets the batch to 2nd Level Review. The completed data review form remains on file.

7.7.4 Reporting Results

Without rounding, enter the raw data into the LIMS. Review the entries. The data book must be compared with the LIMS batch on screen.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and one LCS will be included in each laboratory lot of 20 samples

NOTE: SW-846 Method 9030A describes a quality control sequence that is not followed at STL Chicago, unless specifically required in a QAPP.

8.1.2 The MBs will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine both precision and accuracy.

8.1.3 Accuracy will be measured by the percent recovery of the LCS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, the percent recovery will be plotted on control charts to monitor method accuracy.

8.1.4 Precision will be measured by the reproducibility of the LCS.

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, Project Manager, QA personnel or the laboratory manager.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist and in a non-conformance memo (NCM);
- document on the data review checklist and in an NCM that the system has been brought back within control limits; and
- receive approval (signature) of the supervisor, Project Manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem;

Suggested Actions to specific out of control situations:

8.2.1 Laboratory Control Sample (LCS)

If the LCS is Low:

- when possible, as in a water set, reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure and correct the problem. Soil sets will need to be repeated.

If the LCS is High:

- reanalyze LCS to verify that an out of control situation exists;
- determine the source of contamination or error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be the reagents, the LCS stock solution, or the preparation area.) All samples that are less than the reporting limit may be reported, even though the LCS is high, but the situation must be documented and an NCM must be written.

8.2.2 Method Blank (MB)

- when possible, reanalyze MB to verify contamination at a level > MDL;
- determine the source of contamination and correct the problem;
- all samples above the RL whose concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed. However, note the out-of-control MB on the data review checklist and an NCM must be written.

8.2.3 Matrix Duplicate (MD)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the MDL, then the ± MDL rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- if the reanalysis is still outside of the control limits, note the situation on the data review checklist and on an NCM.

8.2.4 Matrix Spike / Matrix Spike Duplicate (MS / MSD)

- If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis, but must be related properly in any case.
- Report all spikes, whether or not they are in control.
- Note out-of-control spikes on the data review checklist and write an NCM.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Normality of Iodine

$$N = \frac{A \times B}{C}$$

Where:
A = mLs of $Na_2S_2O_3$ titrated (average of 3 titrations)
B = Normality of $Na_2S_2O_3$
C = mLs of Iodine

9.2 Solid Samples

$$\text{mg/kg (wet weight)} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{sample weight (g)}}$$

$$\text{mg/kg (dry weight)} = \frac{\text{mg/kg (wet weight)}}{\text{\% solids (as a decimal)}}$$

Where:
A = normality of iodine
B = mLs of iodine used
C = normality of sodium thiosulfate
D = mLs of sodium thiosulfate

The dry weight correction is made automatically in AD in LIMS, once the % solids is at 2nd Level Review status.

NOTE: The AVS-SEM calculations are done in a separate batch. See Attachment 3.

9.3 Water Samples

$$\text{mg/L} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{sample volume (mLs)}}$$

Where:
A = normality of iodine
B = mLs of iodine used
C = normality of sodium thiosulfate
D = mLs of sodium thiosulfate

9.4 Accuracy

9.4.1 LCS % Recovery

$$\%\ R = \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.4.2 Matrix Spike % Recovery

$$\%\ R = \frac{\text{(spiked sample) - (unspiked sample)}}{\text{spike concentration}} \times 100$$

9.5 Precision

9.5.1 MS/MSD or MD Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Acidic waste generated by the addition of HCl to the samples is disposed of in the corrosive waste stream. The waste does contain zinc, however, zinc is not a toxic metal.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.

13.0 ATTACHMENTS

Attachment 1: Example: Analysis Logbook/LIMS Forms
Attachment 2: Example: Data Review Checklist
Attachment 3: AVS/SEM Work Instruction

Historical File:

Revision 00: 06/19/92
Revision 01: 01/15/93
Revision 02: 03/16/93
Revision 03: 05/13/93
Revision 04: 02/09/95
Revision 05: 10/03/97
Revision 06: 03/31/99
Revision 07: 09/27/00
Revision 08: 03/01/04
Revision 09: 02/21/05
Revision 10: 03/24/06
Revision 11: 03/12/07

Reasons for Change, Revision 11:

- Annual Review
- Add NCM requirement
- Edits made to reflect 2007 40 CFR Rule Change, Section 1.0

Attachment 1.

Example: Analysis Logbook w/ LIMS Forms (023-001 to 023-005)

STL Chicago
Sulfide / Reactive Sulfide

Page #: _____

Normality of I_2:

Trial 1 = _____ mLs
Trial 2 = _____ mLs
Trial 3 = _____ mLs
Avg. = _____ mLs

LabNet Batch # _____
_____

(_____ $_{avg.}$ X N $Na_2S_2O_3$) / 5 = _____
N I_2

N of $Na_2S_2O_3$ = _____

N Check: Date:_____ Book No.:_____ Page No.:_____

Result (mg/L or mg/kg) = (mLs I_2)(N I_2) - (mLs $Na_2S_2O_3$) (N $Na_2S_2O_3$) x 16,000 / Sample Size (mLs or grams)

	Sample #	Test Method	Sample Size	mLs I_2	mLs $Na_2S_2O_3$	% Rec. (RPD)	Comments
	-MB1						
	-LCS1						
	-LCS2						
1							
2							
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
___							
___							

Comments: _____

Standards Traceability

Stock Soln. I ID # (LCS/MS):_____ Standardization: Book_____Page_____

Note: Working standards are prepared daily from noted Stock Solution.

Spiking Levels (mg/L): LCS:_____ MS (Water):_____ MS (Soil):_____

Preparation (Circle): a. Filtered b. Bubbled c. Bubbled with Heat

Prep Analyst:_____ Date/Time: _____

Analyst:_____ Date/Time: _____

Reviewer:_____ Date: _____

023-001

3/28/06 16:37

Sulfide (Titrimetric, iodine)
Method Code..: 376.1
Batch Code...: 176115

Status.....: RVWD
Batch Date...: 03/17/06
Batch Time...: 1432

User Name.....: mtb
QC Code.....: STD
Calc Code.....: SH2O

Location Code..: 57222
Equipment Code.:
Import Code....:

SAMPLE: Grp	Pos	Sample ID	Dilution	TEST CODE / TEST POS Date / Time	SULFID 1	SULH2S 2
1	1	___MB__		3/17/06 1230	0	
1	2	___LCS_I05ISTSF1A_		3/17/06 1233	0	
1	3	245061_2____		3/17/06 1236	0	
1	4	245061_3____		3/17/06 1239	0	
1	5	245061_4____		3/17/06 1242	0	
1	6	245061_5____		3/17/06 1245	0	
1	7	245061_6____		3/17/06 1248	0	
1	8	245061_7____		3/17/06 1251	0	
1	9	245093_2____		3/17/06 1254	0	
1	10	245093_2__MS_I05ISTSF1A_9		3/17/06 1257	N	
1	11	245093_2__MSD_I05ISTSF1A_9		3/17/06 1300	N	
1	12	245093_3____		3/17/06 1303	0	
1	13	245093_15____		3/17/06 1307	0	
1	14	245093_17____		3/17/06 1310	0	
1	15	245093_20____		3/17/06 1313	0	
1	16	245093_27____		3/17/06 1316	0	
1	17	245099_1____		3/17/06 1319	0	0
1	18	245099_2____		3/17/06 1322	0	0
1	19	245099_3____		3/17/06 1325	0	0
1	20	245099_4____		3/17/06 1328	0	0
1	21	245099_5____		3/17/06 1331	0	0
1	22	245099_6____		3/17/06 1334	0	0
1	23	245120_1____		3/17/06 1337		
1	24	245120_2____		3/17/06 1340		

023-002

Sulfide (Titrimetric, iodine) Report Date: 3/28/06 16:37

Method Code..: 376.1 Batch Date...: 03/17/06 QC Code.....: STD Equipment Code.:
Batch Code...: 176115 Batch Time...: 1432 Calc Code.....: SH2O Import Code....:
Status.....: RVWD User Name....: mtb Location Code..: 57222

Grp	Smp	Sample ID	Pos	Test	Result	Known	Original	Alternate	QC Res	F	QC Res	F
1	1	___MB__	1	SULFID	0.1							
1	2	___LCS_I05ISTSF1A_	1	SULFID	4.0	195.3			102			
1	10	245093_2__MS_I05ISTSF1A_9	1	SULFID	8.0	195.3	6.8		31	N		
1	11	245093_2__MSD_I05ISTSF1A_9	1	SULFID	8.2	195.3	6.8	8.0	36	N	14.9	

023-003

Sulfide (Titrimetric, iodine) Report Date: 3/28/06 16:37

Method Code..: 376.1 Batch Date...: 03/17/06 QC Code.....: STD Equipment Code.:
Batch Code...: 176115 Batch Time...: 1432 Calc Code.....: SH2O Import Code....:
Status.....: RVWD User Name....: mtb Location Code..: 57222

SAMPLE:	Grp	Pos	Sample ID	Dilution	SULFID mg/L	SULH2S mg/L	MLI mL	SMPT mL	IODINE mL
	1	1	___MB__		0.1	0.1	250	5.01	5
	1	2	___LCS_I05ISTSF1A_		4.0	4.2	250	2.54	5
	1	3	245061_2____		0.9	1.0	250	4.46	5
	1	4	245061_3____		1.1	1.2	250	4.36	5
	1	5	245061_4____		1.8	1.9	250	3.91	5
	1	6	245061_5____		-0.0	-0.0	250	5.07	5
	1	7	245061_6____		0.5	0.5	250	4.76	5
	1	8	245061_7____		0.3	0.3	250	4.84	5
	1	9	245093_2____		6.8	7.2	250	5.78	10
	1	10	245093_2__MS_I05ISTSF1A_9		8.0	8.5	250	5.03	10
	1	11	245093_2__MSD_I05ISTSF1A_9		8.2	8.7	250	4.90	10
	1	12	245093_3____		6.6	7.0	250	5.96	10
	1	13	245093_15____		11.0	11.7	250	3.16	10
	1	14	245093_17____		-0.6	-0.6	250	5.46	5
	1	15	245093_20____		-2.8	-3.0	250	6.82	5
	1	16	245093_27____		6.6	7.0	250	5.95	10
	1	17	245099_1____		-0.0	-0.0	250	5.07	5
	1	18	245099_2____		0.1	0.1	250	5.01	5
	1	19	245099_3____		0.0	0.0	250	5.05	5
	1	20	245099_4____		0.2	0.2	250	4.96	5
	1	21	245099_5____		0.3	0.3	250	4.90	5
	1	22	245099_6____		0.2	0.2	250	4.93	5
	1	23	245120_1____		0.2	0.2	250	4.95	5
	1	24	245120_2____		-6.0	-6.4	250	8.87	5

023-004

Sulfide (Titrimetric, iodine) Report Date: 3/28/06 16:37

Method Code..: 376.1	Batch Date...: 03/17/06	QC Code.....: STD	Equipment Code.:
Batch Code...: 176115	Batch Time...: 1432	Calc Code.....: SH2O	Import Code....:
Status.....: RVWD	User Name....: mtb	Location Code..: 57222	

SAMPLE:	Grp	Pos	Sample ID	Dilution	NI2 N	NNATHI N	PREPF N/A	DLFAC N/A
	1	1	___MB__		0.0249	0.0246	1.0	1.0
	1	2	___LCS_I05ISTSF1A_		0.0249	0.0246	1.0	1.0
	1	3	245061_2____		0.0249	0.0246	1.0	1.0
	1	4	245061_3____		0.0249	0.0246	1.0	1.0
	1	5	245061_4____		0.0249	0.0246	1.0	1.0
	1	6	245061_5____		0.0249	0.0246	1.0	1.0
	1	7	245061_6____		0.0249	0.0246	1.0	1.0
	1	8	245061_7____		0.0249	0.0246	1.0	1.0
	1	9	245093_2____		0.0249	0.0246	1.0	1.0
	1	10	245093_2__MS_I05ISTSF1A_9		0.0249	0.0246	1.0	1.0
	1	11	245093_2__MSD_I05ISTSF1A_9		0.0249	0.0246	1.0	1.0
	1	12	245093_3____		0.0249	0.0246	1.0	1.0
	1	13	245093_15____		0.0249	0.0246	1.0	1.0
	1	14	245093_17____		0.0249	0.0246	1.0	1.0
	1	15	245093_20____		0.0249	0.0246	1.0	1.0
	1	16	245093_27____		0.0249	0.0246	1.0	1.0
	1	17	245099_1____		0.0249	0.0246	1.0	1.0
	1	18	245099_2____		0.0249	0.0246	1.0	1.0
	1	19	245099_3____		0.0249	0.0246	1.0	1.0
	1	20	245099_4____		0.0249	0.0246	1.0	1.0
	1	21	245099_5____		0.0249	0.0246	1.0	1.0
	1	22	245099_6____		0.0249	0.0246	1.0	1.0
	1	23	245120_1____		0.0249	0.0246	1.0	1.0
	1	24	245120_2____		0.0249	0.0246	1.0	1.0

023-005

Attachment 2.

Example: Data Review Checklist

STL Chicago
INORGANICS – STL LIMS DATA REVIEW CHECKLIST **Test** _____ **Analytical Batch#** _____

Prep Batch # _____
(File by analytical batch #)

Batch Entry Date: _____ Analysis Date: _____ No. of Jobs in Batch: _____

Analyst / Primary Reviewer: _____ 1st Level Review Date: _____

Secondary Reviewer: _____ 2nd Level Review Date: _____

	PRI REV	SEC REV	COMMENTS
1) Analyst correct			
2) Instrument Code present			
3) Was Data Imported _____ Manually entered _____ Balance Interface Used _____			
4) Samples & all QC in order as analyzed?			
5) Sample Date/Time analyzed correct			
6) Reagent Codes present and Amount Spiked correct?			
7) Dilution factors all present and correct?			
8) Are correct Sample ID's used? Are all samples designated with a Blue P?			
9) Are correct QC ID's used? Are all QC designated with a Blue P?			
10) Are all QC correctly related to the samples?			
11) Do all entries match raw data?			
12) Is all QC calculated and are correct flags applied?			
13) Is an NCM needed? ICV, MB, LCS, LCSD, DU, MS, MSD, RPD out; holding time missed			NCM # _____ Approved By: _____ Initials
Raw Data: 1) Is AD Batch # is clearly noted?			
2) Are manual calculations and final results clearly shown?			
3) Are all errors crossed out with single line & initialed and dated?			
4) All unused portions of the page(s) Z'd out?			
5) Is data signed & dated by analyst & reviewer?			

Attachment 3.

Example: AVS/SEM LabNet Work Instruction

STL Chicago

AVS/SEM: LabNet Login / Result Update Instructions

Job Number:

Unit	Method Category	LabNet Method	Reported Tests	Test Matrix	Units	Comments	Additional Comments	LabNet Batch
Sulfide	ISF	AVS	Sulfide	E	mg/Kg	Contains AVS Sulfide mg/Kg result Note: % Solids results are entered in the raw %Solids column and are factored into the DLFAC / PREPF	1. "AVS" Column will be blank as it is not needed. 2. The MS/MSD Reagent Factor needs to have the % Solids backed out. (10 / Smp.Wt. x % Solids as decimal)	
		AVSSUM	AVS Sulfide	E	umoles/g	Contains AVS Sulfide mg/Kg result converted to umoles/g results. Make sure Sulfide mg/Kg is logged in LabNet, but is set **not** to report. Calculation: Sulfide mg/Kg / molecular weight (32.066) = umoles/g	1. Start a New Batch 2. Sample Info Screen - Find Samples; 3. Test Data Screen - Fill Cells and Calculate; 4. Sample Info Screen - Manually enter DLFAC from AVS batch; 5. Report Data Screen - Check Sulfide result column - for **ALL Sulfide Results** that are < MDL, the AVS result column in the Test Data Screen needs to be changed to "0" for the ratio calculation to work properly. This is done **after** the batch has been calculated , and only the calc'd AVS result is changed, not the raw sulfide result. (Note: There is no QC reported in this AV	
ICP	MIL	SEMPRP	SEM Prep	E		Note: % Solids results are entered in the raw %Solids column and are factored into the DLFAC / PREPF	Weight/Final Volume are taken from inorganic preparation weight log book	
		SEMICP	Routine: Cd, Cu, Ni, Pb, Zn Extra Metals: Ag, As, Cr, Sb	E	mg/Kg	Contains SEM Total ICP metals analysis	ICP 'E' Reagent Factor for the LCS/MS/MSD=100	
Hg	MHL	SEMHGP	SEM Prep	E		Note: % Solids results are entered in the raw %Solids column and are factored into the DLFAC / PREPF	Weight/Final Volume are taken from inorganic preparation weight log book	
		SEMHG	Hg	E	mg/Kg	Contains SEM Total Hg metal analysis	Double check that job is logged with mg/Kg units; HG 'E' Reagent Factor for the LCS/MS/MSD=1000	
Calculations	MIL	SEMSUM	SEM Metals SEMSUM of Routine Metals SSEXTR Routine + added Metals	E	umoles/g	SEM mg/Kg Metal results from the SEMICP and SEMHG methods are converted to umoles/g results Calculations: Hg = mg/Kg Hg / 200.59 Cd = mg/Kg Cd / 112.41 Cu = mg/Kg Cu / 63.546 Pb = mg/Kg Pb / 207.2 Ni = mg/Kg Ni / 58.6934 Zn = mg/Kg Zn / 65.39	DLFAC is manually entered in Sample Info Screen from the SEM_Prep Batch; **ALL** non-detect results (below MDL) need to be changed to "0" for the ratio calculation to work properly. This is done **after** the batch has been calculated, and only the calc'd SEM_ SUM result is changed, not the raw result.	
		SEMAVS	AVSSEM: Routine calc. ratio AVSMEX: Routine + added Metals Ratio	E	Ratio	Calculated ratio between (SEMSUM and AVS) or (SSEXTR and AVS)	Do not calculate until all above steps have been checked for completion.	

Note: It is advised to print the sample results out of LabNet before non-detects are changed to "0", as other errors may be caught at this time.
The correct conversion of the mg/Kg results to umoles/g need to be assessed for accuracy.

Reviewer: _____ Date: _____

SOP No.	Revision No.	Date	Page
UWC-353.2_AQ2	00	06/30/06	1 of 20

TITLE: WET CHEMISTRY
Nitrate-Nitrogen by Cadmium Reduction by AQ2 - Seal

Updated by:	Signature:	Date:
Pete Ficarello Wet Chemistry		6/26/06

Approved by:	Signature:	Date:
Diane L. Harper Inorganics Manager		6-26-06
David W. Mazur Env. Health & Safety Coor.		6/26/06
Terese A. Preston Quality Manager		6/25/06

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Full Signature Approvals Are Kept on File
with STLs QA Standard Practice Records

STL BURLINGTON
SOP CHANGE-IN-PROGRESS ATTACHMENT (CIPA)

SOP Title:	DISSOLVED GASES IN GROUNDWATER
SOP Number:	LM-GC-RSK175
SOP Revision:	9
SOP Date Effective:	04/28/06
CIPA Date Effective:	12/29/06

Change Approval Signatures:

QA Manager: Kirstin McCracken **Date:** 12/29/06

Kirstin McCracken

Department Manager: Jacob L. Bailey **Date:** 12/29/06

Jacob L. Bailey

The following revisions or additions in BOLD TEXT were made to the referenced SOP. These changes were implemented on the CIPA Date Effective indicated above.

Section 7.1, Page 3 of 15, insert the following table(s) and text:

Primary Source Matheson Micromat 14 Mix Gas

Component	Concentration	
	%	PPMV
Methane	1	10,000
Ethane	1	10,000
Ethene	1	10,000
Hydrogen	1	10,000
Carbon Dioxide	1	10,000
Acetylene	1	10,000
Carbon Monoxide	1	10,000
Nitrogen	Balance	NA

Primary Source Matheson Micromat 14 Bone Dry CO_2

Component	Concentration	
	%	PPMV
Carbon Dioxide	99.8	998,000

Second Source Standards: Purchase a different manufacturer lot of the primary source standard.

Primary Source CO_2 Working Standard (5% / 50,000 ppmv): Using a gas tight syringe transfer 912.2 mL of the primary source stock CO_2 standard into a 6 L Summa Canister. Pressurize the canister with nitrogen to 29.99976 psig, which corresponds to a final volume of 18.2448 L.
Where:

Second Source CO_2 Working Standard (5% / 50,000 ppmv): Using a gas tight syringe transfer 912.2 mL of the second source stock CO_2 standard into a 6 L Summa Canister. Pressurize the canister with nitrogen to 29.99976 psig Pressurize the canister with nitrogen to 29.99976 psig, which corresponds to a final volume of 18.2448 L.

Section 11.1, Page 6 of 15:

To prepare a MS/MSD for carbon dioxide prepare two additional aliquots of the parent sample and add 1 mL of ~~**Matheson Micromat 14 Gas Mix**~~ **of the primary source 5% CO_2 working standard** into the headspace to yield a spike concentration equivalent to the mid-level calibration standard.

Section 11.2, Page 7 of 15:

For GC/TCD analysis (carbon dioxide), manually inject ~~**300**~~ **500** uL of the standards and samples directly onto the column.

Table 1, Section 18.0, Page 11 of 15:

Table 1: Target Analyte List and Reporting Limit

Compound	CAS Number	Reporting Limit (ug/L)
Methane	000074-82-8	2
Ethane	000074-84-0	4
Ethene	000074-85-1	3
Carbon Dioxide	000124-38-9	~~**500**~~ **1000**

Appendix A: Section 18.0. Page 13 of 15:

The standard formulations contained in this appendix are recommended and are subject to change. If the concentration or volume of any of the stock standard changes, the standard preparation instructions must be adjusted accordingly. See laboratory SOP LP-QA-002 *Standard Preparation* for further guidance.

Prepare separate calibration curves for methane, ethane, ethene and carbon dioxide. A separate calibration curve and source calibration standard must be prepared for carbon dioxide because the Matheson Micromat 14 gas mixture contains hydrogen which co-elutes with carbon dioxide on the column.

Calibration Standard GC/FID (Methane, Ethane, Ethene)

Primary Source Matheson Micromat 14 Gas Mix **(10,000 PPMV)**	Level 1	Level 2	Level 3	Level 4	Level 5
Volume Added (uL)	1.3	50	200	600	1000

Final Concentration (ug/L) Calibration Level 1-5 (Methane, Ethane, Ethene)

Analyte	Level 1	Level 2	Level 3	Level 4	Level 5
Methane	0.47	18	73	218	363
Ethane	0.89	34	136	409	681
Ethene	0.83	32	127	381	636
~~**Carbon Dioxide**~~	~~**500**~~	~~**2500**~~	~~**5000**~~	~~**75000**~~	~~**10000**~~
~~**Acetylene**~~	~~**0.77**~~	~~**30**~~	~~**118**~~	~~**354**~~	~~**590**~~

Calibration Standard GC/TCD (Carbon Dioxide)

~~**Matheson Micromat 14 Gas Mix**~~ **Primary Source CO_2 Working Standard (50,000 PPMV)**	Level 1	Level 2	Level 3	Level 4	Level 5
Volume Added (mL)	~~**0.1**~~ **0.2**	0.5	1.0	1.5	2.0

Final Concentration (ug/L) Calibration Level 1-5 (Carbon Dioxide)

Analyte	**Level 1**	**Level 2**	**Level 3**	**Level 4**	**Level 5**
Carbon Dioxide	~~**500**~~ **1000**	**2500**	**5000**	**75000**	**10000**

ug/L= PPMV of Parent Standard x (molecular weight (g) / 24.47) x (volume added (mL) /18 mL)

Compound	Molecular Weight (g)
Methane	16
Ethane	30
Ethene	28
~~**Acetylene**~~	~~**26**~~
Carbon Dioxide	44

STANDARD OPERATING PROCEDURE
STL BURLINGTON

DISSOLVED GASES IN GROUNDWATER
RSK-175
Applicable Matrix: Groundwater

APPROVAL SIGNATURES

Christopher A. Ouellette
Laboratory Director

Date: April 14, 2006

Kirstin L. McCracken
Quality Assurance Manager

Date: April 14, 2006

Jennifer L. Clements
Department Manager

Date: April 14, 2006

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of dissolved gases (methane, ethane and ethene) in groundwater. This procedure may also be used for the determination of carbon dioxide. This procedure is applicable to the concentration of dissolved gas in headspace. This procedure is not applicable to the determination of total sample concentration (concentration in headspace + concentration in water).

1.2 The target compounds that can be determined by this procedure and their associated Reporting Limits (RL) are listed in Table 1, Section 18.0.

2.0 SUMMARY OF METHOD

2.1. Samples are collected without headspace in 44 mL VOA vials. Samples for methane, ethane and ethane are preserved with hydrochloric acid at the time of collection. Samples for carbon dioxide are not preserved. Prior to analysis the sample is transferred to a 22 mL serum vial with a crimp cap and headspace is created using. Nitrogen. Samples for methane, ethane, ethene are loaded onto a headspace autosampler and analyzed by GC/FID. Samples for carbon dioxide are manually injected and analyzed by GC/TCD.

3.0 DEFINITIONS

3.1 Definitions are included in Appendix B.

4.0 INTERFERENCES

4.1. Non-target compounds from the sample matrix can cause interference, which may result in positive identifications of non-target compounds with retention times similar to those of target compounds. The extent of these interferences will vary depending on the nature of the samples.

5.0 SAFETY

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.1. Specific Concerns or Requirements

The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2. Primary Materials Used

Table 2, Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure**.** A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1. 22 mL serum vials with crimp cap tops.

6.2. Computer Hardware/Software: GC Acquisition Platform- VAX 4505 (GVAX) Multichrom V2.11. Data Processing- Hewlett-Packard 9000-series computers, an HP9000 D250 (Chemsvr4) and an HP 9000 K200 (Chemsvr5)/HP-UX 10.20 and Target V3.5.

6.3. GC/FID/TCD: with dual columns, headspace autosampler, or equivalent.

6.4. GC Columns:

- FID- Rt-UPLOT, (30m x 0.53 mmID)
- TCD- CTR 1, (6 feet inner with porous polymer and 6 feet outer with molecular sieve).

6.5. Syringes-10 uL to 5.0 mL gas tight syringes with Luer-Lok tip.

6.6. Supply of ultrahigh purity argon, helium, hydrogen, and nitrogen.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

VOA Free Reagent Water

7.1. Standards

Stock gaseous standards are purchased from commercial vendors. To prepare each standard, 18 mL of reagent water is added to a 22 mL serum vial. The vial is capped and 4 mL of headspace is generated before an appropriate volume of gaseous standard is added to the vial. The recommended formulation for the preparation of the calibration standards is provided in Appendix A. The procedures for the preparation of continuing calibration verification standard (CCV) and QC samples are provided in Sections 10.0 and 11.0.

8.0 SAMPLE HANDLING AND PRESERVATION

8.1. Samples for analysis of methane, ethane and ethane should be collected in 44 mL VOA vials preserved with 1:1 HCl to a pH of less than 2. Samples for analysis of carbon dioxide should be collected **unpreserved** in 44 mL VOA vials.

8.2. Immediately following collection, samples must be cooled and stored at 4º C ± 2º C until the time of analysis. The holding time is 14 days from time of collection.

8.3. Unless otherwise specified by client or regulatory program, after analysis, samples are retained for a minimum of 30 days after provision of the project report and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1. The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are summarized in Table 3, Section 18.0. Below is a summary of each type of QC sample that is analyzed with the method.

9.2. A Method Blank (MB) and Laboratory Control Sample (LCS) are prepared with each analytical batch. These samples show that the laboratory is in control, independent of the sample matrix.

9.3. A Matrix Spike and Matrix Spike Duplicate (MS/MSD) should be analyzed with each analytical batch if sufficient sample volume is provided. Project specific MS/MSD and Sample Duplicates (SD) are performed per client request. These samples show the effect of the sample matrix on the accuracy and precision of the method.

9.4. Instrumental QC standards include a five-point calibration (ICAL), an Initial Calibration Verification (ICV) standard, also referred to as a second source standard, that contains all target analytes, is analyzed to verify the ICAL standard formulation. Continuing Calibration Verification (CCV) standards are analyzed every 24 hours and at the end of each analytical sequence.

10.0 CALIBRATION AND STANDARDIZATION

10.1. Instrument Operating Conditions

The recommended instrument operating conditions are as follows:

FID:
Temperature Program: 40º for 3.5 minutes
FID Temperature: 200ºC
Injection Port Temperature: 50ºC
Carrier gas: Helium, 30 mL/min
Hydrogen (FID): 30 mL/min
Air (FID): 300 mL/min

TCD:
Temperature Program: 75º for 3.5 minutes
TCD Temperature: 150ºC
Injection Port Temperature: 50ºC
Filament Temperature: 185ºC
Injection Port Temperature:
Carrier gas: Argon, 60 mL/min

10.2. Initial Calibration

Prepare a five-point calibration by adding a volume of gas standard into a 22 mL vial that contains 18 mL of deionized water and 4 mL of headspace. Use UHP nitrogen to create the headspace. The volumes of standard required to prepare each calibration level is provided in Appendix A along with the final concentration of each prepared standard.

Analyze the calibration standards following the procedure that begins in Section 11.2. The data processing system calculates the Calibration Factor (CF), mean CF and Percent Relative Standard Deviation (%RSD). The % RSD for all target analytes must be $\leq$ 30% for the calibration to be considered acceptable. If the %RSD is outside criteria for any target compound, investigate the cause of the problem and correct prior to the analysis of samples.

10.3. Initial Calibration Verification

Immediately following initial calibration, verify the calibration with a second source (ICV) standard.

To prepare the ICV for methane, ethane and ethene, inject 200 uL of the second source gaseous standard into a 22 mL vial that contains 18 mL of VOA free water and 4 mL of headspace to yield an ICV concentration equivalent to CAL Level 3. To prepare the ICV for carbon dioxide, inject 1 mL of the second source gaseous standard into a 22 mL vial that contains 18 mL of VOA free water and 4 mL of headspace to yield an ICV concentration equivalent to CAL Level 3.

Analyze the standard following the procedure that begins in Section 11.2. The percent recovery of the ICV must be 70%-130% recovery of the expected value.

10.4. Continuing Calibration Verification (CCV)

Following the procedure in Section 11.0, prepare and analyze the mid-level CCV every 24 hours and at the end of the analytical sequence. The percent difference of the CCV must be $\pm$30% as compared to the initial calibration. Samples must be bracketed by passing CCVs, and samples before and after CCV failure must be reanalyzed, unless the CCV is high and there are no detects in the associated samples.

10.5. Troubleshooting: The following items can be checked in case of calibration failures:

ICAL Failure: Perform instrument maintenance. In extreme cases, install new columns.

CCV Failure: Perform instrument maintenance.

Auto-sampler failure: Reset the auto-sampler.

Power Failure: Reset run in Multichrom and re-acquire or re-initiate run sequence.

11.0 PROCEDURE

11.1. Sample & QC Preparation

Remove the samples from refrigerated storage and allow them to warm to room temperature. Transfer the sample into a 22 mL vial with a crimp cap. Insert a 22-gauge needle into the septum. Using a 5 mL gastight syringe, inject 4 mL of nitrogen with acetylene into the vial. For carbon dioxide, use UHP nitrogen to create the headspace. The nitrogen forces out an equal amount of sample through the 22-gauge needle to create a headspace volume of 4 mL. Withdraw the needle and syringe from the vial and shake the vial vigorously for several seconds.

To prepare a MS/MSD for methane, ethane and ethane, prepare two additional aliquots of the parent sample and add 200 uL of Matheson Micromat 14 Gas Mix into the headspace to yield a spike concentration equivalent to the mid-level calibration standard.

To prepare a MS/MSD for carbon dioxide prepare two additional aliquots of the parent sample and add 1 mL of Matheson Micromat 14 Gas Mix into the headspace to yield a spike concentration equivalent to the mid-level calibration standard.

To prepare the method blank for methane, ethane and ethene transfer 22 mL of VOA free reagent water into a 22 mL vial and seal with a crimp cap. Insert a 22-gauge needle into the septum. Using a 5 mL gastight syringe, inject 4 mL of nitrogen with acetylene into the vial. The nitrogen forces out an equal amount of water through the 22-gauge needle to create a headspace volume of 4 mL.

To prepare the method blank for carbon dioxide free, transfer reagent 22 mL of VOA free reagent water into a 22 mL vial and seal with a crimp cap. Insert a 22-gauge needle into the septum. Using a 5 mL gastight syringe, inject 4 mL of UHP nitrogen into the vial. The nitrogen forces out an equal amount of water through the 22-gauge needle to create a headspace volume of 4 mL.

To prepare the LCS for methane, ethane and ethene, inject 200 uL of the second source gaseous standard into a 22 mL vial that contains 18 mL of VOA free water and 4 mL of headspace to yield an ICV concentration equivalent to CAL Level 3.

To prepare the LCS for carbon dioxide, inject 1 mL of the second source gaseous standard into a 22 mL vial that contains 18 mL of VOA free water and 4 mL of headspace to yield an ICV concentration equivalent to CAL Level 3.

11.2 Analysis

Arrange the samples in a sequence that begins with the calibration standards (ICAL if necessary or CCV) followed by the analysis of QC samples, field samples and continuing calibration verification standards (CCVs).

Establish the instrument operating conditions and calibrate the instrument(s) in accordance with Section 10.0. If an acceptable initial calibration already exists, begin the sequence with analysis of the continuing calibration verification standard.

For GC/FID analysis (methane, ethane, ethane), place the standards, samples, and blanks onto the Tekmar headspace autosampler and initiate the analytical sequence. The autosampler equilibrates the sample's water and headspace phases at 40°C and injects 100 uL of sample headspace onto the GC column, where target analytes if present are detected by the FID.

For GC/TCD analysis (carbon dioxide), manually inject 300 uL of the standards and samples directly onto the column.

The data system identifies the target analytes by comparing the retention time to the retention times of the mid-point of the initial calibration. The data system calculates the concentration for each target analyte from the calibration curve. If the data system does not properly integrate a peak, perform manual integration. All manual integration must be performed and documented in accordance with laboratory SOP LP-LB-0006 *Manual Integration*.

After analysis is complete, evaluate the results against the performance criteria given in Section 10 and Table 3, Section 18.0 and perform corrective action as necessary.

Dilute and reanalyze samples whose results exceed the calibration range. The diluted analysis should ideally result in a determination within the upper half of the calibration curve.

12.0 CALCULATIONS

12.1 Percent Recovery (%R)

$$\%R = \frac{C_s}{C_n} \times 100$$

Where:
C_s = Concentration of the Spiked Field or QC Sample
C_n = Nominal Concentration of Spike Added

12.2 Percent Recovery for MS/MSD (%R)

$$\%R = \frac{C_s - C_u}{C_n} \times 100$$

Where:
C_s = Concentration of the Spiked Sample
C_u = Concentration of the Unspiked Sample
C_n = Nominal Concentration of Spike Added

12.3 Relative Percent Difference (RPD)

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

Where:
C_1 = Measured Concentration of First Sample
C_2 = Measured Concentration of Second Sample

12.4 Calibration Factor (CF)

$$CF_i = \frac{\text{Peak area or height}_{(x)}}{\text{Standard concentration}_{(ug/L)}}$$

12.5 Mean Calibration Factor

$$\overline{CF} = \frac{\sum_{i=1}^{n} CF_i}{n}$$

Where: n = number of calibration levels

12.6 Standard Deviation of the Calibration Factor

$$SD = \sqrt{\frac{\sum_{i=1}^{n} \left(CF_i - \overline{CF}\right)2}{n-1}}$$

Where: n = number of calibration levels

12.7 Relative Standard Deviation of the Calibration Factor (%RSD)

$$\%RSD = \frac{SD}{\overline{CF}} \times 100$$

12.8 Percent Difference (CCV)

$$\%D = \frac{CF_v - \overline{CF}}{\overline{CF}} \times 100$$

Where: CF_v = Calibration Factor from the Continuing Calibration Verification (CCV)

12.9 Sample Concentration

$$Concentration = \frac{Ax}{CFav} \otimes DF$$

Where:
Ax = Peak area of analyte
CFav = Mean calibration factor

13.0 DATA ASSESSMENT, CORRECTIVE ACTION & REPORTING

13.1 Data Review and Corrective Action

Review the samples, standards and QC samples against the acceptance criteria in Table 3. If the results do not fall within the established limits, perform the recommended corrective action. If corrective action is unsuccessful, document the situation with a nonconformance report and/or qualify the data using an appropriate data qualifier (see Appendix C for data qualifier definitions). For additional guidance regarding the laboratory's protocol and required elements for each level of data review refer to laboratory SOP LP-LB-003 *Data Review*.

13.2 Data Reporting

The laboratory's RL for each target analyte is provided in Table 1. Report the data to the RL adjusted for sample dilution/concentration. The reporting limit is the threshold value below which results are reported as non-detected. Report sample results that have concentrations for a target analytes less than the RL with a "U" qualifier.

Some projects may require reporting positively identified target analytes less than the RL. In this case, the analyte can be qualitatively detected but not accurately quantified. Flag all results less than the RL with a "J" data qualifier (Appendix C).

Some projects may require RLs that are less than the laboratory's routine RL. Sample results may be reported to the project RL if the project RL is greater than the Quantification Limit (QL) and above the MDL. In this context, the QL is defined as the

concentration of the low calibration standard. If the project RL is less than the QL, all values less than the QL must be reported as estimated and qualified with a "J".

Further guidance on the application and use of the MDL, RL, and QL is provided in laboratory SOP LP-LB-009 *Determination of Method Detection Limits.*

13.3 Data Management and Records: All electronic and hardcopy data is managed, retained, and archived as specified in laboratory SOP LP-QA-0014 *Laboratory Records*.

14.0 METHOD PERFORMANCE

14.1 A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009 *Method Detection Limits.*

14.2 A demonstration of analyst capability (IDOC) is required before use of this SOP and any time there is a significant change in instrument type, personnel or test method.

14.3 Employee Training, and IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training*.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in Section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

The following waste streams are produced when this method is carried out.

- Acidic Sample Waste / Satellite Container: 5 Gallon Plastic Bucket

15.2 Transfer the waste stream to the satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations, The procedures for waste management are further given in the laboratory SOP LP-LB-001 *Hazardous Waste.*

16.0 REVISION HISTORY

16.1 Title Page: Revised to reflect current management structure. The SOP number was changed from LM-AT-RSK175 to LM-GC-RSK175.

16.2 Sections 1.0 to 15.0: All sections were revised to describe current laboratory practice.

16.3 Section 16.0: Renamed revision history (formerly references)

16.4 Section 17.0: Renamed references (formerly tables, diagrams, flowcharts)

16.5 Section 18.0: Inserted as tables, diagrams and flowcharts.

17.0 REFERENCES

17.1. Method RSK-175, Revision 0, August 1994.

18.0 TABLES, DIAGRAMS,FLOWCHARTS.

18.1 Table 1:Target analyte list, Reporting Limits
18.2 Table 2: Primary Materials Used.
18.3 Table 3: QC Summary, Frequency, Acceptance Criteria and Corrective Action
18.4 Appendix A: Standard Preparation Tables
18.5 Appendix B: Definitions
18.6 Appendix C: Equations

Table 1: Target Analyte List and Reporting Limit

Compound	CAS Number	Reporting Limit (ug/L)
Methane	000074-82-8	2
Ethane	000074-84-0	4
Ethene	000074-85-1	3
Carbon Dioxide	000124-38-9	500

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: QC Summary

QC Item	Frequency	Acceptance Criteria	Recommended Corrective Action
ICAL	Before sample analysis, when CCVs indicate calibration is no longer valid, after major instrument maintenance.	CF: RSD ≤ 30%	Correct problem, reanalyze, repeat calibration.
ICV	After each initial calibration	%R (70-130)	Correct problem and verify second source standard. If that fails, repeat initial calibration.
CCV	Every 24 hours and at the end of the sequence	%D ± 30%	Re-analyze once, if still outside criteria perform corrective action, sequence can be re-started if two successive CCVs pass, otherwise repeat ICAL and all associated samples since last successful CCV, unless CCV is high and bracketed samples are non-detects.
MB	Every 20 samples	< RL DoD: ≤ ½ RL	Examine project DQO's and take appropriate corrective action, which may include re-analysis of MB, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. If there are no detects in samples, or if all detects are > 10 X MB level, re-prep and reanalysis may not be required.
LCS	Every 20 samples	%R (70-130)	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.
MS/MSD SD	Every 20 samples if sufficient sample volume is available. Project specific MS/MSD and SD per client request	%R (70-130) RPD < 30	Examine project DQO's and take appropriate corrective action, which may include re-analysis of LCS, re-extraction of batch, and/or non-conformance report (NCR). Corrective action must be documented on NCR. Flag all reported values outside of control limits.

Appendix A: Calibration Standard Preparation Tables

The standard formulations contained in this appendix are recommended and are subject to change. If the concentration or volume of any of the stock standard changes, the standard preparation instructions must be adjusted accordingly. See laboratory SOP LP-LB-002 *Standard Preparation* for further guidance.

Calibration Standard GC/FID (Methane, Ethane, Ethene)

Matheson Micromat 14 Gas Mix	Level 1	Level 2	Level 3	Level 4	Level 5
Volume Added (uL)	1.3	50	200	600	1000

Calibration Standard GC/TCD (Carbon Dioxide)

Matheson Micromat 14 Gas Mix	Level 1	Level 2	Level 3	Level 4	Level 5
Volume Added (mL)	0.1	0.5	1.0	1.5	2.0

Final Concentration

Compound	Level 1	Level 2	Level 3	Level 4	Level 5
Methane	0.47	18	73	218	363
Ethane	0.89	34	136	409	681
Ethene	0.83	32	127	381	636
Carbon Dioxide	500	2500	5000	75000	10000
Acetylene	0.77	30	118	354	590

Formula : ug/L= PPMV x (MW/24.47) x (mL injected/18mL)

Where:
MW = Molecular Weight

Compound	Molecular Weight (g)
Methane	16
Ethane	30
Ethene	28
Acetylene	26
Carbon Dioxide	44

Appendix B: Terms and Definitions

Acceptance Criteria: specified limits placed on characteristics of an item, process or service defined in requirement documents.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator.

Analyte: The specific chemicals or components for which a sample is analyzed. (EPA Risk Assessment Guide for Superfund, OSHA Glossary).

Batch: environmental samples that are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria. An analytical batch is composed of prepared environmental samples (extracts, digestates and concentrates), which are analyzed together as a group.

Calibration: a set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring instrument or measuring system, or values represented by a material measure or a reference material and the corresponding values realized by the standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

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

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

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

Data Qualifier: a letter designation or symbol appended to an analytical result used to convey information to the data user. (Laboratory)

The qualifiers that are routinely used for this test method are:

U: Compound analyzed for but not detected at a concentration above the reporting limit.
B: Compound is found in the sample and the associated method blank.
E: Compound whose concentration exceeds the upper limit of the calibration range.
D: Concentration identified from a dilution analysis.
X,Y,Z: Laboratory defined flags that may be used alone or combined as needed. If used, provide a description of the flag in the project narrative.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Matrix Spike Duplicate (MSD): a second replicate matrix spike

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample (QC): a sample used to assess the performance of all or a portion of the measurement system.

1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) is used to determine the amount of nitrogen as nitrate-nitrite in a given sample. Nitrate-nitrogen alone can be determined by subtracting the nitrite-nitrogen amount determined by a separate procedure. This SOP was written using EPA 600/4-79-020 Method 353.2; Standard Methods, 20th Ed., Method 4500-NO_3F. The soil extraction procedure is from EPA Method 300.0. The AQ2 Seal Auto Analyzer is used in place of the Technicon Auto Analyzer described in the method.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DOD Version 3.0 are located in Attachment 3. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project-by-project basis.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. The laboratory maintains reporting limits that are higher than the MDL. Wherever possible, reporting is limited to values ~3-5x the respective MDL to ensure confidence in the value reported.

Matrix	Reporting Limit
Waters	0.1 mg-N/L
Wastes	1 mg-N/kg

1.1.3 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.2 Summary of Method

A clear sample is passed back and forth through a copperized cadmium coil to reduce nitrate-nitrogen to nitrite-nitrogen. The nitrite-nitrogen (that originally present plus reduced nitrate-nitrogen) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured colorimetrically.

2.0 INTERFERENCES

- Residual chlorine can oxidize the cadmium coil and reduce its efficiency.
- Low results may be obtained from samples containing high amounts of iron, copper or other metals. The addition of EDTA in the buffer helps reduce this interference.
- Samples containing high amounts of organics, including oil and grease, will coat the cadmium coil. Pre-extraction with an organic solvent should be performed on these samples.
- Turbidity should be removed by filtration through a 0.45 mm pore diameter membrane prior to analysis.
- True color may result in false positives, and may be corrected for by passing the sample through the flow-cell without the addition of the reagents and manually subtracting the result from the reacted sample result.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

Proper disposal procedures for cadmium need to be followed due its extreme toxicity.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Chloroform	Carcinogen Irritant	50 ppm Ceiling	Acts as a relatively potent anesthetic. Irritates respiratory tract and causes central nervous system effects, including headache, drowsiness, dizziness. Causes skin irritation resulting in redness and pain. Removes natural oils. May be absorbed through skin. Vapors cause pain and irritation to eyes. Splashes may cause severe irritation and possible eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Phosphoric Acid	Corrosive	1 Mg/M3 TWA	Inhalation is not an expected hazard unless misted or heated to high temperatures. May cause redness, pain, and severe skin burns. May cause redness, pain, blurred vision, eye burns, and permanent eye damage.
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
1 – Always add acid to water to prevent violent reactions. 2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 EQUIPMENT AND SUPPLIES

4.1 Seal AQ2 Auto Analyzer

Refer to the instrument manual for set-up instructions. These conditions can be adjusted to optimize instrument conditions.

4.2 Glassware/Miscellaneous

- Disposable sample cups
- Disposable 5 cc syringes
- 0.45 mm filters (syringe or membrane)
- 100 mL volumetric flasks
- Eppendorf pipets and tips
- Reagent wedges
- Reaction segments

5.0 REAGENTS AND STANDARDS

All standards and reagents are prepared with Type II Deionized (DI) Water, unless otherwise stated, in Class A volumetric flasks. Subtle differences exist among the methods referenced regarding the exact preparation and composition of the various reagents used in this test. The following are taken from the Seal procedure.

5.1 Reagents

5.1.1 Sulfanilamide Color Reagent

To ~ 300mLs DI water in a 500 mL volumetric flask, add 19 mLs 85% phosphoric acid, 7.5 grams of sulfanilamide, 0.375 grams of N-(1-naphthyl)ethylenediamine dihydrochloride, and 85 mL of Ammonium Chloride Buffer (see 5.1.2). Dissolve the mixture by stirring on a stir plate and dilute to volume with DI water.

- Life of Reagent: 1-month
- Storage Requirements: Store in an amber bottle in the dark.

5.1.2.1 Ammonium Chloride Buffer

To 800 mLs DI water contained in a 1-L volumetric flask, dissolve 240 grams of ammonium chloride (NH_4Cl) and 1-g disodium ethylenediamine tetracetatetic acid dihydrate ($Na_2EDTA{\cdot}2H_2O$). Use a stir plate; it will take at least 1 hour for the ammonium chloride to dissolve. Adjust the pH to 8.5 with sodium hydroxide and dilute to volume with DI water.

- Life of Reagent: 1-year
- Storage Requirements: None

5.1.2.2 Working buffer

Add 100 uL of 10% (w/v) Triton X-100 solution to 25 mL of ammonium chloride buffer. Shake well to mix.

Life of Reagent: 1-week
Storage Requirements: None

5.1.3 1 N Sodium Hydroxide

To ~600 mLs of DI water in a 1-L volumetric flask, slowly dissolve 40-grams of sodium hydroxide. Swirl to dissolve/mix. Cool. Dilute to volume with DI water.

- Life of Reagent: 1-year
- Storage Requirements: Store in a plastic bottle.

5.1.4 2% Copper Sulfate

To ~800 mLs DI water in a 1-L volumetric flask, add 20-grams of copper sulfate ($CuSO_4 \cdot 5H_2O$) to. Mix and dilute to volume with DI water.

- Life of Reagent: 1-year
- Storage Requirements: None

5.1.5 50% Hydrochloric Acid

Slowly add an amount of hydrochloric acid to an equal amount of water in a glass flask.

- Life of Reagent: 1-year
- Storage Requirements: None

5.2 Standards

5.2.1 Nitrate Stock Solution 1, 100 mg N /L

5.2.2 Nitrate Stock Solution 2 * , 100 mg N /L

To a 1-L volumetric flask containing ~800 mLs DI water, add 0.722-grams of potassium nitrate (KNO_3) and 2 mLs chloroform ($CHCl_3$). Mix and dilute to volume with DI water.

Alternately, a 1 to 1000 dilution of the IC Nitrate Stock I and Stock II may be performed. Neither a further dilution before analysis nor a new LIMS naming convention is necessary for this preparation.

- Life of Standard: 6-months
- Storage Requirements: Keep refrigerated

*Stock 2 is prepared as Stock I **EXCEPT** an alternate stock source is used.

5.2.3 Nitrite Stock Solution 3, 100 mg N/L

To a 1-L volumetric flask containing ~800 mLs DI water, dissolve 0.607-grams of potassium nitrite (KNO_2). Preserve with 2 mLs chloroform ($CHCl_3$). Mix and dilute to volume with DI water. Alternately, 0.4298-grams of sodium nitrite ($NaNO_2$) can be used.

Alternately, a 1 to 1000 dilution of the IC Nitrite Stock I Standard may be performed. Neither a further dilution before analysis nor a new LIMS naming convention is necessary for this preparation.

- Life of Standard: 6-months
- Storage Requirements: Keep refrigerated

5.2.4 Calibration Standards

(Prepared fresh daily – only needed if a manual curve is used. Normally, the 2.0 standard is placed in the Seal autosampler, and the instrument prepares the curve using operator-programmed dilutions.)

Use volumetric flasks to prepare the following standards.

Daily Standard ID	Conc. (ppm)	Percent of High Std.	Volume of Standard 1 (Rgt. 5.2.1)
A	2.0	100	2 mLs diluted to 100 mLs DI Water
B	1.5	75	1.5 mLs diluted to 100 mLs DI Water
C	1.0	50	1 mL diluted to 100 mLs DI Water
D	0.5	25	0.5 mLs diluted to 100 mLs DI Water
E	0.2	10	0.2 mLs diluted to 100 mLs DI Water
F	0.1	5	0.1 mLs diluted to 100 mLs DI Water
G	0.0	0	100 mLs DI Water

5.2.5 Quality Control Standards

Quality Control	Volume of Standard 2 (Rgt. 5.2.2)
Init. Calib. Verification (ICV) (1.0 mg/L)	1.0 mL to 100 mLs DI Water
Lab Control Sample (LCS) (1.0 mg/L)	1.0 mL to 100 mLs DI water
Matrix Spike (MS) (1.0 mg/L)	1.0 mL to 100 mLs Sample
Cont. Calib. Verification (CCV) (0.5 mg/L)	0.5 mLs to 100 mLs DI Water

5.2.6 1.0 ppm Nitrite Standard for Column Efficiency

Dilute 1000 uL of Nitrite Stock Solution 3 (Rgt. 5.2.3) to volume with DI water in a 100 mL volumetric flask so the final concentration is 1.0 ppm. Analyze in sequence (See Section 7.4).

6.0 Calibration (Non-Daily)

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Frequency [1]	Control Limit [2]
Method Blank (MB)	1 in 20 samples	< Reporting Limit
LCS [3]	1 in 20 samples	80 - 120%
MS/MS Duplicate (MSD) [4]	1 in 20 samples	75 - 125%; 20RPD
Matrix Duplicate (MD) [5]	1 in 20 samples	20 RPD

[1] Drinking Water samples are analyzed in sets of 10 with a MD and MS performed on the drinking water matrix. Control limits are ≤10 RPD for duplicates and ±10% recovery for the LCS and MS.
[2] Statistical control limits are available for those clients or projects that require the use of statistical limits. Client-specific QAPs may include QC limits and frequency requirements that supersede those given above.
[3] LCS Duplicate (LCD) is performed only when insufficient sample is available for the MS/MSD or when required by the client/project/contract.
[4] The MS/MSD are the routinely performed matrix QC indicators. The sample selection for matrix QC, if not predesignated by the client, is rotated among client samples so that various matrix problems may be noted and/or addressed.
[5] Matrix Duplicate (MD) is performed only when required by the client/project/contract.

7.2 Sample Preservation and Storage

Sample containers, preservation techniques, and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Samples should be preserved to a pH < 2. Listed below are the holding times and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA) and the Safe Drinking Water Act (SDWA).

Regulation	Holding Time	Preservation[1]	Reference
CWA	28 days	4 mL 48% H_2SO_4/L	40 CFR, Part 136.3
SDWA	28 days	4 mL 48% H_2SO_4/L	EPA 600/4-79-020

[1]All samples are stored at 4 ± 2°C. If Nitrate-as-Nitrogen is to be determined, an unpreserved sample aliquot is required for the nitrite determination, which has a 48-hour hold time.

7.3 Sample Preparation

7.3.1 Sample Size

Matrix	Sample Size
Wastes	10 g/100 mLs DI water
Sludges & Oils	10 g/100 mLs DI water *
Waters	10 mLs

*More sample may be used for sludges high in water content when a low dry weight reporting limit is required.

7.3.2 Cadmium Coil Regeneration

7.3.2.1 Only perform this first step if the cadmium coil has been dried out or fouled by an oily or greasy sample and you are having trouble with reduction efficiency! Remove the coil and flush 5 to 10 mL of 50% HCl through the coil followed by DI water. Let air enter the coil as you are flushing through the water. This helps eliminate debris. When replacing the coil, make sure the ends of the cadmium tube are sitting flush against the Teflon tubing. **Don't perform this unless extremely necessary-because the HCl strips a small layer of cadmium and changes the inner diameter of the cadmium tubing! (see 7.5) Always try regenerating the coil a second time before stripping it with HCl!**

7.3.2.2 Fill reagent wedge 15 with the 2% copper sulfate solution, wedge 14 with the high NO3 standard, and wedge 13 with ammonium chloride buffer.

7.3.2.3 Under the maintenance menu select the icon for coil regeneration. There is a prompt to make sure the proper reagents are ready. Click OK and the coil will automatically be regenerated. This takes approximately 5 minutes.

Note: Make sure reaction segments are in place. If the first segment is 1 and all reaction segments are clean, the sampling needle has trouble dispensing the reagents. If all segments are clean, you could first run an extra reagent wash with DI water, then proceed with the coil regeneration.

7.3.5 Water Sample Preparation

- Adjust sample pH to between 5 and 9 with phenolphthalein indicator, 10N sodium hydroxide, and 5N sulfuric prior to analysis.
- If the sample is turbid, filter through a 0.45 um membrane filter prior to analysis.
- If oil & grease is present, extract the sample with hexane prior to analysis.

7.3.6 Waste/Soil Sample Preparation

- Weigh at least 10 g of sample (to the nearest 0.1 g) into a 250-mL snap-cap vial. Add 100 mLs of DI waters and shake on a wrist-action shaker for 10 minutes.
- Adjust sample pH to between 5 and 9 with concentrated hydrochloric acid or ammonium hydroxide prior to analysis.
- Filter the sample through a glass fiber filter, then through a 0.45 um membrane filter.
- If oil & grease is present, extract the filtrate with hexane prior to analysis.

7.4 Calibration / Standardization

Calibration Controls	Sequence	Control Limit
Standard Curve	prior to samples	±10%
Correlation Coefficient	prior to samples	≥ 0.995
Nitrite Column Efficiency Std. [1]	prior to samples/prior to ICV/ICB	90 - 110%
Initial Calibration Verification (ICV)	prior to samples/after calibration	90 - 110%
Alternate-concentration ICV	Prior to samples/after calibration	90 – 110%
Initial Calibration Blank (ICB)	prior to samples/after calibration	< Reporting Limit
Continuing Calibration Verif. (CCV)	every 10 readings-alternating conc.	90 - 110%
Continuing Calibration Blank (CCB)	every 10 readings	< Reporting Limit

[1] When the column efficiency standard recovery is calculated against the ICV concentration, the acceptance limits of 90 - 110% must be met as well.

7.5 Preventive Maintenance

- Follow the maintenance schedule in the AQ2 manual.
- Occasionally check the cadmium coil volume by running dye indicator as if it were a sample. The dye should be visible passing both ends of the coil as it is being flushed back and forth. If not, go into the test parameters screen for Nitrate 2 in the AQ2 software and adjust in small increments the "Cadmium flush volume". Run the dye indicator again to verify the dye is flushing back and forth properly.

7.6 Sample Analysis (Refer to AQ2 software manual for further explanation)

7.6.1 Turn on instrument and let it warm up for at least an hour. Fill up reagent wedges with appropriate reagent, and replace reaction segments if necessary. Also fill the water bottle with fresh water.

7.6.2 Perform "Daily Startup" in the *Settings* menu. This will prime the syringe, wash the cuvette, and perform water baselines. All the water baselines for filters 1-7 should be between 3.0-9.0 volts. If not, the instrument should still be functional as long as the wavelength being used is within range, but take note of this for it could mean there is a problem, and the voltage may need to be manually adjusted if problems occur.

7.6.3 Double click "Scheduling" and select a tray number for the run. Tray numbers which are currently in use and not yet archived may not be used!

7.6.4 Enter the appropriate sample ID's and types in the order to be run for all of the samples and QC. All regular samples and sample spikes will have the type U. Enter ICV, CCV, ICB, CCB, MB, and LCS codes in both the Type and the ID columns. If running a manually-made curve, cups 1-7 will be the curve standards. If running an auto curve, leave cup 1 empty and start entering the samples and QC in cup 2, beginning with the ICV. We must also run a reduction efficiency check (usually prior to ICV), which is a nitrite standard. If nitrite reduction efficiency check fails, try regenerating coil again.

7.6.5 Enter the test requested by highlighting the all test boxes for all the samples and click the test (NO3). If an automatic dilution is desired, click NO3 twice while on the appropriate sample, and the AQ-2 will dilute and run this sample based on the default dilution factor. If a manual dilution has already been done, click on the *Cup Dilution* box, and this will run the sample as is, but multiply the result by the default dilution factor. Upon completion of all of the run data entry, save this tray.

7.6.6 Fill the 57-place wheel according to the tray just scheduled. Fill the cups most of the way; they only hold ~2mL. Screw down the wheel once samples are poured. If running an auto curve, fill cup 1 with your high standard.

7.6.7 Double click the "Run" button and click on the desired tray. Make sure **Auto Standardization** is checked if running an auto curve, and check **Zero Reaction Segments** if they are all clean. An additional screen will pop-up called *Reagent Volumes*. Make sure all the reagents for nitrate have a number greater than 10 mL (~40) or else the instrument won't run.

7.6.8 To check the curve while the set is running, you can click on "Calibration" and go to the appropriate test and date. If running an auto curve, the instrument will automatically run a carryover check before reading your ICV. Samples can be run without running a curve, and the AQ-2 will calculate all the results based on the last curve ran. Also, if any samples are over-range, the AQ-2 will automatically dilute them based on the default dilution factor and rerun them at the end of the run.

7.6.9 If the run needs to be stopped because QC is out or a dilution needs to be performed, click the red slash button near the top of the window and tell the instrument to "Perform an orderly stop".

7.6.10 Once the run is over or if the instrument was stopped by the analyst and needs to be restarted, double click the "Acceptance" button and select the tray you would like to view. Here the analyst can reschedule samples, reschedule samples with a manual or automatic dilution, and reschedule the curve. Remember when rescheduling samples to also reschedule CCVs and CCBs when necessary.

7.6.11 If the run is over and all samples and QC are ready to be reported, highlight all samples in the *Acceptance* screen and click the "Accept" or "Accept All" buttons. This will archive the tray, and now this tray number can be reused at a future time.

7.6.12 To print a report, click the "Reporting" button, check what should be included in the report (raw data, schedule, etc.), select the date and tray, and click "Generate Report." Calibration curves can be printed from the *Calibration* screen. A **.csv** file is also created when a tray is archived, so print this out also from the AQ-2\Audittrail folder.

7.7 Documentation

7.7.1 Analysis Logbook

The analysis of samples and standards is documented within the instrument runlog (Attachment 1) and supported by the instrument print-out. The runlog must be completed for each day's analysis.

7.7.2 Traceability of Standards

Upon receipt or preparation, each standard, or other reagent is entered into LIMS and is issued a unique ID#. Further information entered into the database includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., Nitrate Stock Solution – LCS/MS). Once the record is created, a unique label is printed and affixed to the appropriate container.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment 2). Upon the first 100% review, the checklist is initialed and dated as reviewed. The package, with its checklist and any documented comments, is submitted to the section manager or peer reviewer for a second review. Once again, the checklist is initialed and dated by the second reviewer. The completed data review checklist remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 At least one MB and LCS will be included in each laboratory lot of 20 or fewer samples. The MB will be examined to determine if contamination is being introduced in the laboratory. The MB and LCS must be carried through all stages of the sample preparation and measurement steps.

8.1.2 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be within control limits (Section 7.1) in order to be considered acceptable.

8.1.3 Precision will be measured by the reproducibility of the MSs and will be calculated as Relative Percent Difference (RPD). If MSs were not analyzed, precision will be measured using the LCS/LCD. The recoveries must be within control limits in order to be considered acceptable.

8.1.4 One MS/MSD is performed per matrix per 20 sample analytical set (unless otherwise required by the method).

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out-of-control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out-of-control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, QA personnel, project manager or the lab manager.

Steps that must be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a the data review checklist;
- document on that an in-control situation has been achieved; and
- receive approval (signature) of the Section Manager, QA personnel, Project Manager or the Laboratory Manager prior to the release of any analytical data associated with the problem.

QC Indicator	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare new stock and/or working standards; • check reagents/solutions and prepare fresh if necessary.
ICV	• reanalyze the ICV to verify proper preparation; • prepare a new ICV from the original stock; • check for instrument base-line drift; • restandardize with existing standards, reanalyze; • check reagents/solutions and prepare fresh if necessary; • prepare new stock and/or working standards and recalibrate;
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc.... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

QC Indicator	Suggested Corrective Actions
LCS	• reanalyze the LCS to verify that an out of control situation exists; • if the re-reading of the LCS confirms the contamination or low recovery, determine the source of error, correct the problem and repeat the sample set. (Sources of error include but are not limited to the preparation or mixing of the standard solution, faulty distillation technique, or ammonia contamination in Milli-Q or distillation apparatus); and; • if the recovery of the LCS is high, all non-detected sample results may generally be reported; • Note any out-of-control situations on the data review checklist.
MB	• Reanalyze the MB to verify contamination at a level > Reporting Limit; • Determine the source of contamination and correct the problem; • All samples whose detected nitrate concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which a non-detect or is >10 times the MB level need not be reanalyzed; • Note any out-of-control situations on the data review checklist.
MS	• The spiked sample must be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times; • If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis. For LabNet to report matrix QC it MUST be reported in the same batch as the original sample analysis. • Report all spikes, whether or not they are in control. • Note out-of-control spikes on the data review checklist.
CCV	• reanalyze the CCV to verify proper preparation; • prepare a new CCV from original stock; • check for instrument base-line drift; • check reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all samples since the previous in control CCV; • never dispose of any samples until you are sure that all QC are within their designated control limits.
CCB	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources). • never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Terminology

- N_2N_3-N: Total nitrogen in the form of nitrate-nitrogen and nitrite-nitrogen obtained directly from the auto analyzer.
- NO_3-N: Nitrate-nitrogen, N_3N_2 after correction for NO_2-Nitrogen obtained from EPA Methods 354.1 or 300.0. The nitrite result can also be obtained from the Seal by bypassing the reduction coil, but this is rarely performed at STL Chicago due to the 48-hour holding time and laboratory logistics.

9.2 Concentration

N_3N_2-N mg/L = N_3N_2-N (mg N/L curve) x dilution factor

NO_3-N mg/L = N_3N_2-N (mg N/L) - NO_2 (mg/L)

$$N_3N_2\text{-N mg/kg} = \frac{N_3N_2\text{-N (mg N/L curve)}}{\text{sample wt. (g)}} \times \text{final volume (mLs)} \times \text{dilution factor}$$

NOTE: All dry weight corrections are made in LabNet at the time the final report is prepared.

$$\textbf{9.3 Column Efficiency} = \frac{1.0\text{ mg N/L } N_3N_2\text{-N observed}}{1.0\text{ mg N/L } NO_2\text{-N observed}} \times 100$$

9.4 Accuracy

$$\textbf{9.4.1 ICV/CCV, LCS \% Recovery} = \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$$

9.4.2 Matrix Spike % Recovery =

$$\frac{\text{(spiked sample conc.) - (unspiked sample conc.)}}{\text{spiked concentration}} \times 100$$

9.5 Precision

9.5.1 Relative Percent Difference (RPD)

$$RPD = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

9.6 Reporting Results

Without rounding, enter the raw data into LIMS (or export the file to LIMS). Review the entries. The data book, instrument print-out, and LIMS entries must be reviewed by the analyst and a trained reviewer using the appropriate data review checklist prior to releasing the data for reporting purposes.

10.0 Waste Management and Pollution Control

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- The waste generated by the Seal auto-analyzer during nitrate analysis may contain traces of cadmium, and other unknown contaminants. The waste is line fed to the Heavy Metal Corrosive Waste Water carboy located in the cabinet under the instrument.
- The waste generated by the auto diluter is line fed into the Waste Water carboy located in the cabinet beneath the instrument.
- Contaminated disposable glassware and plasticware utilized for the analysis is to be placed in the Non-Hazardous, white, solid waste collection bins.

11.0 Method Performance Criteria

Refer to sections 1, 6, 7 and 8.

12.0 References

Refer to Section 1.0

13.0 ATTACHMENTS

Attachment 1: Example: Analysis Run Log w/ LIMS Forms / Maintenance Log
Attachment 2: Example: Data Review Checklist
Attachment 3: DoD QSM Version 3: Appendix DOD-B QC Requirements Summary (Table B-1)

Historical File:

Revision 00: 03/30/06		

Reasons for Change, Revision 00:

- New SOP for AQ2 Seal instrumentation

U:\QC\SOP\UWC\UWC-353_2_AQ2.doc

Attachment 1.

Example: Analysis Run Log w/ LIMS Forms / Maintenance Log

STL Chicago

Nitrate-Nitrite

Page #: _____

Instrument: _____ Wavelength: 520 nm Chord: Full ___ Other ___ Book #: _____

Method: a. EPA 353.2 Cell Path Length: 1.0 cm Channel: 1 ___ 2 ___ 3 ___

b. SM 4500NO3F

Drinking Water Set: _____ Beginning Time: _____ LabNet Batch: _____

Column Efficiency: _____ End Time: _____ Clone Batch(s): _____

Sample #	Sample Size g / mls	Anal. Dil.	Re-Analysis Required	Comments
ICV				% Rec
ICB				mg/L
CCV1				% Rec
CCB1				mg/L
CCV2				% Rec
CCB2				mg/L
CCV3				% Rec
CCB3				mg/L

Sample #	Sample Size g / mls	Anal. Dil.	Re-Analysis Required	Comments
CCV4				% Rec
CCB4				mg/L
CCV5				% Rec
CCB5				mg/L
CCV6				% Rec
CCB6				mg/L

Standard Traceability (Working standards are prepared daily from the noted Stock Solutions.)

Stock 1 (Standard Curve); 1000 mg/L: _____

Stock 2 (ICV/CCV/LCS/MS); 1000 mg/L: _____

Stock 3 (NO2 Efficiency Check): _____

LACHAT Maintenance / Method Troubleshooting Notes:

_____

_____

_____

_____

_____

CHI-22-12-018/E-05/02

Analyst Signature: _____ Date: _____

Reviewer Signature: _____ Date: _____

Nitrogen, NO2, NO3 (Auto Cd Red.) | Status.....: RVWD | User Name.....: pmf | Location Code..: 57222
Method Code..: 353.2 | Batch Date...: 06/21/06 | QC Code.....: STD | Equipment Code.: AQ2
Batch Code...: 183763 | Batch Time...: 1453 | Calc Code.....: N3N2 | Import Code....:

			TEST CODE	NO3	NO3NO2
SAMPLE: Grp Pos	Sample ID	Dilution	TEST POS Date / Time	1	2
1 1	___ICAL_I06ASTNN1_				0
1 2	___ICV_I06CSTNN2_		6/21/06 1434		0
1 3	___ICB__		6/21/06 1436		0
1 4	___MB__		6/21/06 1438		0
1 5	___LCS_I06CSTNN2_4		6/21/06 1439		0
1 6	246979_5____		6/21/06 1441		0
1 7	246979_12____		6/21/06 1443		0
1 8	246979_12__MS_I06CSTNN2_7		6/21/06 1445		0
1 9	246979_12__MSD_I06CSTNN2_7		6/21/06 1446		0
1 10	247006_1____	10	6/21/06 1448		0
1 11	247006_2____	10	6/21/06 1450		0
1 12	247140_6____	500	6/21/06 1452	0	
1 13	247140_7____	500	6/21/06 1453		
1 14	___CCV_I06CSTNN2_		6/21/06 1455		0
1 15	___CCB__		6/21/06 1457		0

Nitrogen, NO2, NO3 (Auto Cd Red.) Report Date: 6/25/06 8:34

Method Code..: 353.2 Batch Date...: 06/21/06 QC Code.....: STD Equipment Code.: AQ2
Batch Code...: 183763 Batch Time...: 1453 Calc Code.....: N3N2 Import Code....:
Status.....: RVWD User Name....: pmf Location Code..: 57222

Grp	Smp	Sample ID	Pos	Test	Result	Known	Original	Alternate	QC Res	F	QC Res	F
1	1	___ICAL_I06ASTNN1_	2	NO3NO2		100						
1	2	___ICV_I06CSTNN2_	2	NO3NO2	1.0459	100			105			
1	3	___ICB__	2	NO3NO2	-0.0004							
1	4	___MB__	2	NO3NO2	0.0014							
1	5	___LCS_I06CSTNN2_4	2	NO3NO2	0.9999	100	0.0014		100			
1	8	246979_12__MS_I06CSTNN2_7	2	NO3NO2	1.2130	100	-0.0179		121			
1	9	246979_12__MSD_I06CSTNN2_7	2	NO3NO2	1.2355	100	-0.0179	1.2130	124		2.4	
1	14	___CCV_I06CSTNN2_	2	NO3NO2	0.5169	100			103			
1	15	___CCB__	2	NO3NO2	-0.0012							

Nitrogen, NO2, NO3 (Auto Cd Red.) Report Date: 6/25/06 8:34

Method Code..: 353.2	Batch Date...: 06/21/06	QC Code.....: STD	Equipment Code.: AQ2
Batch Code...: 183763	Batch Time...: 1453	Calc Code.....: N3N2	Import Code....:
Status.....: RVWD	User Name....: pmf	Location Code..: 57222	

BATCH:	Item	Description	Description Information
	1	Comments	
	2	Comments	
	3	Comments	
	4	Comments	

SAMPLE:	Grp	Pos	Sample ID	Dilution	NO3 mg/L	NO3NO2 mg/L	NO2RAW mg/L	N32RAW mg/L	MLI mL
	1	1	___ICAL_I06ASTNN1_						
	1	2	___ICV_I06CSTNN2_			1.0459		1.0459	
	1	3	___ICB__			-0.0004		-0.0004	
	1	4	___MB__			0.0014		0.0014	
	1	5	___LCS_I06CSTNN2_4			0.9999		0.9999	
	1	6	246979_5____			-0.0128		-0.0128	
	1	7	246979_12____			-0.0179		-0.0179	
	1	8	246979_12__MS_I06CSTNN2_7			1.2130		1.2130	
	1	9	246979_12__MSD_I06CSTNN2_7			1.2355		1.2355	
	1	10	247006_1____	10		1.2380		1.23799	
	1	11	247006_2____	10		1.4190		1.41902	
	1	12	247140_6____	500	1.6992	1.6992	0.0000	1.69924	
	1	13	247140_7____	500	1.6380	1.6380	0.0000	1.6380178	
	1	14	___CCV_I06CSTNN2_			0.5169		0.5169	
	1	15	___CCB__			-0.0012		-0.0012	

SAMPLE:	Grp	Pos	Sample ID	Dilution	MLF mL	WEIGHT g	PREPF N/A	DLFAC N/A	
	1	1	___ICAL_I06ASTNN1_				1.0	1.0	
	1	2	___ICV_I06CSTNN2_				1.0	1.0	
	1	3	___ICB__				1.0	1.0	
	1	4	___MB__				1.0	1.0	
	1	5	___LCS_I06CSTNN2_4				1.0	1.0	
	1	6	246979_5____				1.0	1.0	
	1	7	246979_12____				1.0	1.0	
	1	8	246979_12__MS_I06CSTNN2_7				1.0	1.0	
	1	9	246979_12__MSD_I06CSTNN2_7				1.0	1.0	
	1	10	247006_1____	10			1.0	1.0	

Nitrogen, NO2, NO3 (Auto Cd Red.) Report Date: 6/25/06 8:34

Method Code..: 353.2	Batch Date...: 06/21/06	QC Code.....: STD	Equipment Code.: AQ2
Batch Code...: 183763	Batch Time...: 1453	Calc Code.....: N3N2	Import Code....:
Status.....: RVWD	User Name....: pmf	Location Code..: 57222	

SAMPLE:	Grp	Pos	Sample ID	Dilution	MLF mL	WEIGHT g	PREPF N/A	DLFAC N/A	
	1	11	247006_2____	10			1.0	1.0	
	1	12	247140_6____	500			1.0	1.0	
	1	13	247140_7____	500			1.0	1.0	
	1	14	___CCV_I06CSTNN2_				1.0	1.0	
	1	15	___CCB__				1.0	1.0	

A1. Daily - Prior to Analysis:

Refill water bottle with fresh water
Perform 10 primes with Cd Coil ticked (*remember to untick if not performing Cd reduction*)
Check cuvette fan operation
Check aspiration bubbles
Perform "Daily Startup"-this will prime syringe, wash cuvette, and perform waterbaselines. *Note of any baselines that are "Out of Limit"!!*

A2. Daily - After Analysis

Perform extra reagent wash with
1. 50% Isopropanol
2. Acid flush
3. EDTA solution

Non-Routine Maintenance is performed on an as needed basis and is documented in the Comments Section of the Daily Maintenance Log the recommended type/frequency of this type of maintenance is listed below.

B. Weekly

Clean aspiration needle
Clean sampler needle
Check wasteflow
Check diluter function
Clean washwell

C. Monthly

Check peristaltic pump tubing
Realign mechanical settings

D. As needed

Replace lightbulb
Replace peristaltic pump tubing
Replace syringe
Replace aspiration needle, etc.

General Information:

Date:							
Analyst Initials:							
Parameter(s):							

Prior to Analysis:

Refill water bottle							
Perform 10 primes w/Cd coil on							
Check cuvette fan							
Check aspiration bubbles							
Perform "Daily Startup"							

After Analysis:

Wipe Any Spills							
Wash with 3 different reagent washes							

Comments:

Reviewer Signature:_____ Date:_____

Page: _____

Attachment 2.

Example: Data Review Checklist

STL Chicago
INORGANIC CLP / LEVEL IV DATA REVIEW CHECKLIST

Site Name: _____ Primary Reviewer: _____ Review Date:_____
JOB Number: _____ Secondary Reviewer: _____ Review Date:_____
No. of Samples/Matrix: a) WATER _____ b) SOIL _____ c) TCLP / SPLP _____ d) OTHER _____

Metals List: a) TAL b) PP c) TCLP d) Other (_____)
Report Level: **IDL** = a) CLP b) Non-CLP c) MDL d) Other _____ **CRDL** = a) CLP b) Client c) Default RL d) Other _____

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LAB CHRON: 1) Matches COC			
2) Proper Prep Links: S-F6 (Routine) S-F9 (TCLP/SPLP)			
3) Sample Hold Times Met			
Cyanide Reported on Forms	Y / N		Method: a) CLP b) SW846 9010B/9014
Initial / Continuing Calibration Criteria Met (CRA/CRI requirements met if applicable)			
FORM 1: Matches Report LabNet Report Units / Test Matrix Match Form 1's Dilutions due to interference's resulted in elevated RL's			
FORM 3: Method Blanks < CRDL			
FORM 5A: MS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			N
FORM 5B: PDS Performed			
FORM 6: Duplicate RPD Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			*
FORM 7: LCS Recoveries Acceptable Default Limits _____ Statistical Limits _____ Project Limits _____ (S-F10 used to Clone By Project)			^
FORM 8: MSA Analysis Performed			S
GFAA – Analytical Spike (AS) Recoveries Acceptable			W
GFAA – Repeat Analytical Recovery <40%			E
GFAA – Duplicate Injection Precision Met			M
FORM 9: Serial Dilution (SD) Acceptable			E
FORM 14's Correct			
RAW DATA: Complete (Match Batches to LabChron) a) Instr. Raw Data clearly displays the LabNet Batch number and includes the "Batch Worksheet" Report b) Prep Raw Data displays the LabNet Batch Number and includes the "Batch Worksheet" Report or "Raw Data" Report			

Comments on Reverse

TASK : CAR's _____	PRI REV	SEC REV	COMMENTS
LabNet Batch Status Report Displays Data At RVWD Status			
Incomplete JOB Status Report reveals no Outstanding Data			
NARRATIVE: 1) Holding Times			
2) Method References			Method: a) CLP b) SW846 c) Other
3) % Recoveries / RPD's			
4) Analytical Difficulties/Typos			

COMMENTS:

QC CYCLE	REASON
1	
2	

STL Chicago
INORGANICS – STL LIMS DATA REVIEW CHECKLIST **Test** _____ **Analytical Batch#** _____

Prep Batch # _____
(File by analytical batch #)

Batch Entry Date: _____ Analysis Date: _____ No. of Jobs in Batch: _____

Analyst / Primary Reviewer: _____ 1st Level Review Date: _____

Secondary Reviewer: _____ 2nd Level Review Date: _____

	PRI REV	SEC REV	COMMENTS
1) Analyst correct			
2) Instrument Code present			
3) Was Data Imported _____ Manually entered _____ Balance Interface Used _____			
4) Samples & all QC in order as analyzed?			
5) Sample Date/Time analyzed correct			
6) Reagent Codes present and Amount Spiked correct?			
7) Dilution factors all present and correct?			
8) Are correct Sample ID's used? Are all samples designated with a Blue P?			
9) Are correct QC ID's used? Are all QC designated with a Blue P?			
10) Are all QC correctly related to the samples?			
11) Do all entries match raw data?			
12) Is all QC calculated and are correct flags applied?			
13) Is an NCM needed? ICV, MB, LCS, LCSD, DU, MS, MSD, RPD out; holding time missed			NCM # _____ Approved By: _____ Initials
Raw Data: 1) Is AD Batch # is clearly noted?			
2) Are manual calculations and final results clearly shown?			
3) Are all errors crossed out with single line & initialed and dated?			
4) All unused portions of the page(s) Z'd out?			
5) Is data signed & dated by analyst & reviewer?			

Attachment 3:

DoD QSM Version 3: Appendix DOD-B QC Requirements Summary (Table B-1)

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Inorganics (WC)

QC Check	Definition	Purpose	Evaluation
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Distilled Standards (one high and one low) (Cyanide only)	Standards are run through the distillation procedure and then compared to the undistilled standards' reported values	To check the efficiency of the distillation process.	Results must agree to within ± 15 % of the undistilled value before analysis can proceed
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of interest. The ICAL must be successful before any samples or other QC check samples can be analyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.
Matrix Verification sample (CR+6 only)	A pH adjusted filtrate that has been spiked with CR+6 eo ensure that the sample matrix does not have a reducing condition or other interferents that could affect color development	To ensure that the sample matrix does not have a reducing condition or other inteferents that affect color development	To verify the absence of an interference, the spike recovery must be between 85% and 115%. If the result of the verification indicates a suppressive intereference, the sample should be diluted and reanalyzed. If the interference persists after the sample dilution, an alternate method should be used.
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
RT window width calculate for each analyte and surrogate (non-MS chromatographic methods only)	Determine the length of time between the sample injection and the appearance of a peak at the detector. The total length of time (window) is established for each analyte or groups of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.	To ensure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the standards and sample matrix to be analyzed. It is done to minimize the occurrence of both false positive and false negative results	Used to evaluate continued system performance. Tight RT windows may result in false negatives and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide RT windows may result in false positive results that cannot be confirmed upon further analysis.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

SEVERN TRENT STL

DETRMINATION OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY
EPA METHOD 524.2, Revision 4.1
Applicable Matrix: Potable Water
Standard Compound List and Reporting Limits: See Table 1

APPROVAL SIGNATURES

Laboratory Director: Michael F. Wheeler, Ph.D. Date: 6/11/04

QA Manager: Kirstin L. McCracken Date: 6-10-04

Department Manager: Bryce E. Stearns Date: 6/11/04

Proprietary Information Statement:

1.0 SCOPE AND APPLICATION

1.1. This SOP describes the laboratory procedure used for the determination of volatile organic compounds in potable water. This procedure is applicable to a wide range of organic compounds that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures.

1.2. The list of compounds that can be determined by this procedure is given in Table 1 along with the reporting limit and characteristic quantitation ions.

2.0 SUMMARY OF METHOD

2.1. Volatile organic compounds and surrogates are purged from the aqueous sample by bubbling an inert gas (helium) through a 5 mL sample aliquot. The purged sample components are trapped in a sorbent tube, which is heated and back flushed with helium to desorb the trapped components into a gas chromatography (GC) column interfaced to a mass spectrometer (MS). A temperature program is used to separate the target analytes, which are subsequently carried on a gas stream into the ion source of the MS. The end of the GC column is positioned so that eluting compounds are immediately ionized and separated according to their mass/charge (m/z) ratio by the quadrapole analyzer. Target compounds are identified by comparing their measured mass spectra and retention times to reference spectra and retention times maintained in the laboratory database. The concentration of target components is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion compound produced by the internal standard.

2.2 This procedure is based on EPA Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1, USEPA Office of Research and Development, 1995.

3.0 DEFINITIONS

3.1. Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1. Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

4.2. Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of

reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during extraction procedures can contribute to sample contamination. Extraction laboratory personnel should not enter the volatile analytical laboratory.

4.4. Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5.0 SAFETY

5.1. Employees must be trained on and adhere to the policies and procedures for safety in the Corporate Safety Manual and this document.

5.2. Safety Concerns or Requirements

Protective clothing such as a lab coat, safety glasses and latex gloves should be worn when performing this procedure.

5.3. Primary Materials Used

Table 2, Section 17.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure. A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Sample Containers: Certified clean, 40 mL screw cap vials each equipped with Teflon faced silicone septum.

6.2 Autosampler: Tekmar ALS 2050, Varian Archon or equivalent.

6.3 Purge & Trap: Tekmar LSC 2000; VOCARB 3000 trap or equivalent

6.4 Gas Chromatograph: Hewlett-Packard 5890 Series II or equivalent.

6.5 Mass Spectrometer: Hewlett-Packard 5971 MSD, Hewlett-Packard 5972 MSD, Hewlett-Packard 5973 MSD, or equivalent.

6.6 Column: Fused silica capillary column, J&W DB624 75 m x 0.53 mm x 3.0 um or equivalent.

6.7 Syringes

- 250 µL - 10 mL glass gas tight hypodermic syringes with Luer-Lok tip
- Micro syringes 10 uL, 100 µL

6.8 Data System: Hewlett-Packard Chem Server and processing software Target 3.5 (or most current version), HP Chem Station software (instrument control and acquisition).

6.9 Standard Storage Containers: 1 - 5 mL Mininert Teflon lined screw caps

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Trap Packing Material: VOCARB 3000 or equivalent.

Methanol: Purge and Trap Grade.

Reagent water: Deionized water filtered through the laboratory's Milli Q plus ™ filtration system, boiled for one hour and purged with helium for at least fifteen minutes. The reagent water must be stored in clean, narrow-mouth bottles equipped with Teflon lined septa and screw caps.

Hydrochloric acid (1+1): Carefully ad a measured volume of concentrated HCl to an equal volume of reagent water.

Ascorbic Acid: ACS reagent grade

Sodium Thiosulfate: ACS reagent grade

7.2 Standards

Custom ISTD Mix #50684: A custom standard solution purchased commercially from Restek. The solution includes fluorobenzene, chlorobenzene-d_5 and 1,4-Dichlorobenzene-d_4 each at a concentration of 1000 ug/mL.

Custom SSTD Mix #53837: A custom solution standard purchased commercially from Restek. The solution includes 1,2-Dichloroethane-d4, BFB, Toluene-d8, 1,2-dichlorobenzene-d4 each at a concentration of 2000ug/mL.

BFB Tune Verification Standard: A stock standard solution of 4-Bromofluorobenzene purchased commercially from Restek at a concentration of 5000ug/mL, CAT#30003.

Primary Dilution Standard: Prepare from stock standard solutions in purge and trap grade methanol using the following "recipe":

20 uL Restek SSTD Mix #53837
20 uL Restek 524 Mix 8 #30203
20 uL Restek 524 Mix 7B #30202B
20 uL Restek Mega Mix #30431
20 uL Restek Gases #30042
100 uL Restek 524 Mix 7A #30202A
544 uL STL 524 Fort Mix
3256 uL P&T Grade Methanol

Store the prepared standard with minimal headspace and check the solution frequently for signs of deterioration or evaporation. The expiration date for the primary dilution standard, when stored at 0°C with minimal headspace, is one month or sooner if it is determined that deterioration or evaporation has occurred.

The final concentration of target analytes in the prepared primary dilution standard solution is 10 ug/mL except for those compound noted in the following table:

Analyte	Final Concentration ug/mL
Tert-butyl Alcohol	1000
Group A	
Acetone	50
2-butanone	50
2-hexanone	50
4-methyl-2-pentanone	50
Tetrahydrofuran	50
Group B	
1-1-dichloropropanone	200
2-nitropropane	200
Group C	
Chloroacetonitirile	500
Nitrobenzene	500
Proprionitrile	500

Internal Standard Solution (25 ug/mL): Dilute 150 uL of Custom ISTD Mix #50684 in 6.0 mL of methanol. The prepared standard is stable for one month when stored at 0°C. Add 3.5 uL of the prepared solution to each 44 mL VOA vial containing sample, standard, and blank to achieve a final concentration of 2 ug/L.

Calibration Standards: Prepare a series of five calibration standards by adding the appropriate volumes of the primary dilution standard and internal standard solution to 44mL VOA vials filled with VOA free reagent water using the recipe given in the following table. Store the calibration standards at 4 °C and prepare fresh daily.

Calibration Level	Concentration ug/L	Primary Dilution Standard (10-500 ug/mL)	Internal Standard Mix 25 ug/mL
Level 1	0.5	2.2	3.5 uL
Level 2	2.0	8.8	3.5 uL
Level 3	10	44	3.5 uL
Level 4	20	88	3.5 uL
Level 5	30	132	3.5 uL

The concentration of the prepared standards is given below:

Concentration→ (ug/L)	Routine	Group A	Group B	Group C	Tert-butyl alcohol
Level 1	0.5	2.5	10	25	50
Level 2	2.0	10	40	100	100
Level 3	10	50	200	500	200
Level 4	20	100	400	1000	500
Level 5	30	150	600	1500	1000

Surrogate Standard Solution (25 ug/mL): Dilute 75 uL of Custom SSTD Mix #53837 in 6.0 mL of methanol. The prepared standard is stable for one month when stored at 0 °C. Add 3.5 uL of the prepared solution to each 44 mL VOA vial containing sample, QC and blank to achieve a final concentration of 2 ug/L.

LCS/MS Standard Solution: Prepare from stock standard solutions obtained from a different lot than those used to prepare the primary dilution standard in purge and trap grade methanol using the following "recipe":

20 uL Restek SSTD Mix #53837
20 uL Restek 524 Mix 8 #30203
20 uL Restek 524 Mix 7B #30202B
20 uL Restek Mega Mix #30431
20 uL Restek Gases #30042
100 uL Restek 524 Mix 7A #30202A
544 uL STL 524 Fort Mix
3256 uL P&T Grade Methanol

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection

All samples should be collected in 44 mL vials in triplicate. If samples such as finished drinking water, are suspected to contain residual chlorine (TRC), 25 mg of ascorbic acid (per 5mg/L of TRC) should be added to the sample container before sample collection. If analytes that are gases at room temperature (such as vinyl chloride) are not to be determined then sodium thiosulfate (STS) should be used to reduce residual chlorine; 3mg of STS per 5mg/L TRC should be sufficient.

A field reagent blank (FRB) should be utilized with each sample set. Prepare the FRB(s) in triplicate by filling a blank sample container with reagent water and preservatives. Overfill the vial prior to closure to prevent the formation of air bubbles. Seal the container and ship to the sampling site with the empty sample containers. The FRB must remain sealed until the time of analysis.

When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes). Adjust the water flow to about 500 mL/min and collect triplicate samples containing the desired preservative. Fill the vials to closure to prevent the formation of air bubbles.

When sampling from an open body of water, partially fill a 1-quart wide-mouth bottle or 1-L beaker with sample from a representative area and fill triplicate sample containers that include the desired preservative from the larger container.

Fill sample bottles taking care not to flush out the preservative or dechlorinating agent. No air bubbles should pass through the sample as the bottle is filled or be trapped in the sample when the bottle is sealed.

8.2 Preservation

Adust the pH of the sample to < 2 at the time of the collection by adding two drops of 1:1 HCl for each 40 mL of sample. Alternatively, for non-chlorinated water sources, pre-preserved sample vials may be used. Ensure that the vials are overfilled prior to closure, then seal the sample containers with the Teflon side to the sample and mix for one minute. Do not mix the ascorbic acid or sodium thiosulfate directly with the HCl in the sample container prior to sampling.

Note: When sampling for THM analysis only, the acidification step may be omitted if sodium thiosulfate is used to dechlorinate the sample.

If a sample foams vigorously when HCl is added, discard the sample and recollect without acidification. These samples must be analyzed within 24 hours of collection.

After collection, all samples must be chilled to about 4°C and maintained at that temperature until analysis. Pack field samples in sufficient ice to ensure that they arrive at the laboratory with a substantial amount of ice remaining in the cooler in order to maintain the thermal preservation requirement.

8.3 Storage and Holding Times

Store samples at a temperature of $\leq 4\pm2$°C in a storage area free of organic solvent vapors and direct or intense light.

The holding time for preserved samples is fourteen days from date of collection and unpreserved samples should be analyzed within 24 hours of collection but the laboratory cannot guarantee that the 24-hour holding times can be met.

9.0 QUALITY CONTROL

9.1 QC Requirements

The following QC samples are analyzed with each analytical batch: Laboratory Reagent Blank (LRB), and Laboratory Fortified Blank (LFB). A Laboratory Fortified Matrix (LFM), Field Duplicates (FD) Field Reagent Blanks (FRB) and Laboratory Duplicates (LD) are performed per client request.

In addition to calibration (ICAL), instrument standardization is checked with the following: Tune Standard (BFB), Continuing Calibration Verification (CCV) and a Quality Control Sample (QCS). The LFB analyzed with each sample set is a second source standard that is also analyzed after each calibration to serve as the QCS. Sample results that exceed the linear range are diluted and reanalyzed. The minimum frequency requirements, acceptance criteria and recommended corrective action for QC samples are provided in Table 5, Section 17.0.

All samples (field and QC) reagent blanks, and calibration standards are fortified with surrogate and internal standard solutions to achieve a concentration in sample of 2 ug/L.

The following surrogate compounds are used:

- 1,2-Dichlorethane-d4
- 1,2-Dichlorobenzene-d4
- 4-Bromofluorobenzene
- Toluene-d_8.

The following internal standards may be used. Table 4, Section 17.0 lists the internal standards assigned to each target compound.

- Fluorobenzene,
- Chlorobenzene-d_5
- 1,4-Dichlorobenzene-d_4.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Tune Standard (BFB)

Prior to the acquisition of a calibration curve or the analysis of samples, analyze and evaluate a (4-Bromofluorbenzene) tune standard using the same instrument operating conditions that are used for calibration and sample analysis (See 11.2). Manually inject a 1 uL aliquot of the 25 ug/L tune standard onto the GC and evaluate the BFB peak spectrum is evaluated against the criteria given in Table 3. The ion abundances shown in Table 3 must be met before analysis of calibration standards may proceed.

10.2 Initial Calibration (ICAL, QCS/LFB)

After the BFB and prior to the analysis of samples, calibrate the instrument with the calibration solutions that were prepared as per Section 7.2. Purge the solutions using the procedure given in Section 11.2.

The data system calculates a response factor (RF) for each target analyte and isomer pair for each calibration level using the appropriate internal standard. See Table 1 for the quantitation ions used for all compounds. For each analyte and surrogate, the data system calculates the mean response factor from analyses of the calibration solutions and calculates the standard deviation (SD) and relative standard deviation (RSD) from each mean. The %RSD must be less than or equal to 20% for the calibration to be considered acceptable. If the criteria are not met, perform instrument maintenance and repeat the calibration procedure.

After calibration, verify the calibration by analyzing the QCS/LFB. The percent recoveries for each analyte of interest msut be 70-130% and the absolute areas of the quantitation ions of the internal standards and surrogates must not have decreased by more than 30% from the areas measured in the most recent continuing calibration check or by more than 50% from the areas measured during the initial calibration.

10.3 Continuing Calibration (BFB & CCV)

Verify the tune and initial calibration every 12 hours during which samples are analyzed.

Analyze and evaluate a BFB (4-Bromofluorbenzene) tune standard using the same instrument operating conditions that are used for calibration and sample analysis (See 11.2). Manually inject a 1 uL aliquot of the 25 ug/L tune standard onto the GC and evaluate the BFB peak spectrum is evaluated against the criteria given in Table 3. The ion abundances shown in Table 3 must be met before analysis of calibration standards may proceed.

Prepare the CCV from the same standard source as the calibration standard at a nominal concentration equivalent to the Level 2 calibration standard (2ug/L). Purge and analyze the CCV using the same procedure and conditions that were used for initial calibration. Vary the concentration of the CCV over time to ensure that the instrument is reliable over the entire working range of the calibration.

For the continuing calibration to be considered acceptable, the RF for each analyte and surrogate must be within 30% of the mean value measured from the initial calibration. (Table 4) and the absolute areas of the quantitation ions of the internal standards and surrogates must not have decreased by more than 30% from the areas measured in the most recent continuing calibration check or by more than 50% from the areas measured during the initial calibration. If these criteria are not met, perform instrument maintenance and recalibrate.

11.0 PROCEDURE

11.1 Sample Preparation

Allow samples to warm to room temperature. Add 3.5 uL of the internal standard solution (25 ug/L) and surrogate solution (25 ug/L) to each 44 mL sample vial. Add 8.8 uL of LCS standard solution to each sample designated as the laboratory fortified matrix (LFM) to achieve a nominal LFM concentration of nominally 2 ug/L.

To prepare the laboratory reagent blank (VBLK): Fill a 5 mL syringe or a 44mL with reagent water taking care to ensure that there are no air bubbles. Add 3.5 uL of the internal standard solution (25 ug/L) and surrogate solution (25 ug/L) through the Luer Lok valve or the septa.

To prepare the laboratory fortified blank (LFB or LCS): Spike 4.4uL of the LCS standard solution into a vial containing 44mL of VOA free lab water. This preparation results in a nominal LCS concentration of 1 ug/L. Add 3.5 uL of the internal standard solution (25 ug/L) and surrogate solution (25 ug/L).

11.2 Sample Introduction, Purging, and Data Acquisition

Arrange the field and QC samples in the autosampler, which is set to transfer 5 mL of sample to the purge vessel.

Alternatively, the samples may be manually injected directly into the purge vessel once the appropriate volume of internal standard and surrogate solution have been added.

Check to ensure that the temperature of the trap is at 30°C then purge the sample for 11 minutes at ambient temperature.

After the 11 minute purge, rapidly preheat the trap to 240°C and place the purge and trap in the desorb mode. Simultaneously start the follow of helium, raise the trap temperature to 250°C and being data acquisition. While the trapped components are being introduced into the gas chromatograph, the automated sampling system drains and washes the purge vessel twice with reagent water.

Acquire and store the data over the nominal mass range 35-300 with a total cycle time (including scan overhead time) of two seconds or less. The cycle time is adjusted to measure five or more spectra during the elution of each GC peak. A typical multi-stage temperature ramp is used to separate the components of interest for this analysis.

The recommended GC temperature program is as follows:

Initial temperature: 40° C, initial time 4 min.
Ramp1: 7° C/min. to 100° C, hold for 1 min.
Ramp2: 4.2° C/min. to 120° C, hold for 0 min.
Ramp3: 28° C/min. to 220° C, hold for 2.1 min.

After desorbing the sample for four minutes, recondition the trap by returning the purge and trap system to the purge mode. Maintain the trap temperature at 260°C for approximately seven minutes. After 7 minutes, turn off the trap heater and allow it to cool. Once the trap has reached the 30°C set point begin to analyze the next sample.

11.3 Identification of Analytes & Data Analysis

Identify target analytes in a sample by comparing its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. The GC retention time of the sample component should be within three standard deviations of the mean retention time of the compound in the calibration mixture.

In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes are examples of structural isomers that may not be resolved on the capillary columns. These two compounds will be reported as an isomeric pair.

Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks. Subtraction of the concentration in the blank from the concentration in the sample is not performed.

Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. If the response for any analyte exceeds the linear range of the calibration, dilute and reanalyze the sample.

The data system calculates analyte and surrogate concentration from the initial calibration using the equations given in Section 12.0. To calculate the concentration of total trihalomethanes, sum the 4 individual trihalomethane concentrations.

Method 524.2 does not include reporting of tentatively identified compounds (TIC). However, upon request, the laboratory will evaluate for and report up to 15 TICs. Since internal standard and surrogate controls are evaluated in the same context (area response) and these controls are introduced at the same point in the analysis and at the

same concentration (2 µg/L), both the internal standard and surrogate controls are used for TIC quantitation. Chromatographic peaks, not attributable to target analytes, having a peak area ≥ 25% of the nearest internal standard or surrogate will be evaluated as a TIC.

12.0 CALCULATIONS

12.1 Calibrated Compound Concentration

$$C_{(x)} = \frac{A_{(x)} * C_{(IS)}}{A_{(IS)} * \overline{RRF}} * DF$$

Where:
$C_{(x)}$ = Concentration of compound (µg/L)
$C_{(IS)}$ = Concentration of associated internal standard (µg/L).
DF = Dilution Factor.
$A_{(IS)}$ = Area of quantitation ion for associated internal standard.
$A_{(x)}$ = Area of quantitation ion for compound.

$\overline{RRF}$ = Average Relative Response Factor from calibration standard.

12.2 TIC Concentration

$$C_{(x)} = \frac{C_{(is)} A_{(x)}}{A_{(is)} RF} \; DF$$

Where:
$C_{(x)}$= Concentration of Unknown (µg/L).
$C_{(IS)}$= Concentration of nearest internal standard or surrogate (µg/L).
DF = Dilution Factor
$A_{(x)}$ = Area of Unknown
$A_{(IS)}$= Area of associated internal standard.

$\overline{RF}$ = Response Factor-assumed value of 1

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the performance criteria given in Table 5. If the results do not fall within the established limits or criteria, perform corrective action. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 A demonstration of analyst capability (IDOC) is required prior to use of this SOP and any time there is a significant change in instrument type, personnel or test method. IDOC procedures are further described in laboratory SOP LP-QA-011, *Employee Training.*

14.2 A Method Detection Limit (MDL) Study is performed at initial method set-up and subsequently once per 12 month period. A Instrument Detection Limit (IDL) study is performed at initial set up and subsequently every 6 months. The procedure and acceptance criteria for MDL studies are given in laboratory SOP LP-LB-009, *Method Detection Limits & Instrument Detection Limits.* MDL and IDL studies are kept on file by the QA Department.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Waste is disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention." The laboratory procedures for waste management are described in SOP LP-LB-001HAZWD.

15.2 Chemists and technicians accumulate hazardous waste in satellite containers located in the work area. Each satellite container is labeled "Hazardous Waste" along with the name of the waste category. The Hazardous Waste Coordinator or designee routinely empties the satellite containers and transfers the waste to the hazardous waste storage room.

16.0 REFERENCES

16.1 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, 40 CFR Part 136, USEPA Office of Water.

16.2 Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, USEPA Method 524.2, Revision 4.1, 1995.

17.0 TABLES, DIAGRAMS AND FLOWCHARTS

17.1 Table 1: Target Compound List, Reporting Limit and Quantitation Ions
17.2 Table 2: Primary Materials Used
17.3 Table 3: BFB Criteria
17.4 Table 4: Internal Standards Assigned for Quantitation
17.5 Table 5: QC Frequency, Criteria and Recommended Corrective Action

Table 1: Target Compound List, Reporting Limit and Quantitation Ions

Compound	CAS #	RL (ug/L)	Characteristic Ions		
			Quant MZ1	Qual MZ2	Qual MZ#
Dichlorodifluoromethane	75-71-8	0.5	85	87	
Chloromethane	74-87-3	0.5	50	52	
Vinyl Chloride	75-01-4	0.5	62	64	
Bromomethane	74-83-9	0.5	94	96	
Chloroethane	75-00-3	0.5	64	66	
Trichlorofluoromethane	75-69-4	0.5	101	103	
Diethyl Ether	60-29-7	0.5	59	45	
1,1-Dichloroethene	75-35-4	0.5	96	61	63
Methyl Iodide	74-88-4	0.5	142	127	
Carbon Disulfide	75-15-0	0.5	76	78	
Allyl Chloride	107-05-1	0.5	41	39	
Methylene Chloride	75-09-2	0.5	84	86	49
Acrylonitrile	107-13-1	0.5	52	53	
trans-1,2-Dichloroethene	156-60-5	0.5	96	61	98
Methyl-t-Butyl Ether	1634-04-4	0.5	73	57	
1,1-Dichloroethane	75-34-3	0.5	63	65	83
2,2-Dichloropropane	594-20-7	0.5	77	97	
cis-1,2-Dichloroethene	156-59-2	0.5	96	98	
Methylacrylate	96-33-3	0.5	55	0	
Bromochloromethane	74-97-5	0.5	128	49	130
Methacrylonitrile	126-98-7	0.5	67	52	
Chloroform	67-66-3	0.5	83	85	
1,1,1-Trichloroethane	71-55-6	0.5	97	99	61
1-Chlorobutane	109-69-3	0.5	56	41	
Carbon Tetrachloride	56-23-5	0.5	117	119	
1,1-Dichloropropene	563-58-6	0.5	75	110	77
Benzene	71-43-2	0.5	78	77	
1,2-Dichloroethane	107-06-2	0.5	62	64	
Trichloroethene	79-01-6	0.5	95	130	132
Dibromomethane	74-95-3	0.5	93	95	174
1,2-Dichloropropane	78-87-5	0.5	63	62	
Methylmethacrylate	80-62-6	0.5	69	99	
Bromodichloromethane	75-27-4	0.5	83	85	
cis-1,3-Dichloropropene	10061-01-5	0.5	75	110	
Toluene	108-88-3	0.5	92	91	
trans-1,3-Dichloropropene	10061-02-6	0.5	75	110	
Ethyl Methacrylate	97-63-2	0.5	69	41	
1,1,2-Trichloroethane	79-00-5	0.5	83	97	85
Tetrachloroethene	127-18-4	0.5	166	168	129
1,3-Dichloropropane	142-28-9	0.5	76	78	
Dibromochloromethane	124-48-1	0.5	129	127	
1,2-Dibromoethane	106-93-4	0.5	107	109	
Chlorobenzene	108-90-7	0.5	112	77	114
1,1,1,2-Tetrachloroethane	630-20-6	0.5	131	133	119
Ethylbenzene	100-41-4	0.5	91	106	

Table 1: Continued

Compound	CAS #	RL (ug/L)	Characteristic Ions		
			Quant MZ1	Qual MZ2	Qual MZ#
m- & p-Xylene	1330-20-7	0.5	106	91	
o-Xylene	95-47-6	0.5	106	91	
Styrene	100-42-5	0.5	104	78	
Bromoform	75-25-2	0.5	173	175	
Xylene (total)	1330-20-7	0.5	106	91	
Isopropylbenzene	98-82-8	0.5	105	120	
Bromobenzene	108-86-1	0.5	156	158	
1,1,2,2-Tetrachloroethane	79-34-5	0.5	83	85	
1,2,3-Trichloropropane	96-18-4	0.5	110	112	
trans-1,4-Dichloro-2-Butene	110-57-6	0.5	53	88	
2-Chlorotoluene	95-49-8	0.5	126	91	
4-Chlorotoluene	106-43-4	0.5	126	91	
n-Propylbenzene	103-65-1	0.5	120	91	
1,3,5-Trimethylbenzene	108-67-8	0.5	105	120	
Pentachloroethane	76-01-7	0.5	167	117	119
Tert-Butylbenzene	98-06-6	0.5	134	91	119
1,2,4-Trimethylbenzene	95-63-6	0.5	105	120	
Sec-Butylbenzene	135-98-8	0.5	105	134	
1,3-Dichlorobenzene	541-73-1	0.5	146	111	148
p-Isopropyltoluene	99-87-6	0.5	119	134	91
1,4-Dichlorobenzene	106-46-7	0.5	146	111	148
1,2-Dichlorobenzene	95-50-1	0.5	146	111	148
n-Butylbenzene	104-51-8	0.5	91	134	
Hexachloroethane	67-72-1	0.5	117	119	201
1,2-Dibromo-3-Chloropropane	96-12-8	0.5	75	155	157
1,2,4-Trichlorobenzene	120-82-1	0.5	180	182	
Hexachlorobutadiene	87-68-3	0.5	225	223	
Naphthalene	91-20-3	0.5	128		
1,2,3-Trichlorobenzene	87-61-6	0.5	180	182	
1,3,5 Trichlorobenzene	108-70-3	0.5	180	182	
Acetone	67-64-1	5	43	58	
2-Butanone	78-93-3	5	72	57	
Tetrahydrofuran	109-99-9	2.5	42	71	72
4-Methyl-2-Pentanone	108-10-1	2.5	58	57	
2-Hexanone	591-78-6	2.5	43	57	
1,1-Dichloropropanone	513-88-2	10	83	63	
2-Nitropropane	79-46-9	10	41	43	
Propionitrile	107-12-0	25	54		
Chloroacetonitrile	107-14-2	25	75	48	
Nitrobenzene	98-95-3	25	77	123	51
Tert-Butyl Alcohol	75-65-0	10	59	41	
Fluorobenzene (IS)		NA	96	70	
Chlorobenzene-d5 (IS)		NA	117	82	119
1,4-dichlorobenzene-d4 (IS)		NA	152	154	115
1,2-dichloroethane-d4 (SS)		NA	65	102	
Bromoflurobenzene (SS)		NA	95	174	176
1,2-dichlorobenzene-d4 (SS)		NA	152	115	154
Toluene-d8 (SS)		NA	98	70	100

IS=Internal Standard SS=Surrogate

Table 2: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Methanol	Flammable Poison Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 3: Tune Standard Criteria

BFB Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
50	15.0-40.0 percent of mass 95
75	30.0-80.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95
173	less than 2.0 percent of mass 174
174	>50.0 percent of mass 95
175	5.0-9.0 percent of mass 174
176	95.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

Table 4: Internal Standards Assigned for Quantitation

Fluorobenzene		Chlorobenzene-d5	
Dichlorodifluoromethane	Carbon Tetrachloride	Dibromochloromethane	tert-Butylbenzene
Chloromethane	1,1-Dichloropropene	1,2-Dibromoethane	1,2,4-Trimethylbenzene
Vinyl Chloride	Benzene	Chlorobenzene	sec-Butylbenzene
Bromomethane	1,2-Dichloroethane	1,1,1,2-Tetrachloroethane	1,3-Dichlorobenzene
Chloroethane	Trichloroethene	Ethylbenzene	p-Isopropyltoluene
Trichlorofluoromethane	Dibromomethane	m- & p-Xylene	1,4-Dichlorobenzene
Diethyl Ether	1,2-Dichloropropane	o-Xylene	1,2-Dichlorobenzene
1,1-Dichloroethene	Methyl Methacrylate	Styrene	n-Butylbenzene
Acetone	Bromodichloromethane	Bromoform	1,2-Dibromo-3-Chloropropane
Methyl Iodide	Chloroacetonitrile	Xylene (total)	1,2,4-Trichlorobenzene
Carbon Disulfide	cis-1,3-Dichloropropene	Isopropylbenzene	Hexachlorobutadiene
Allyl Chloride	1,1-Dichloropropanone	Bromobenzene	Naphthalene
Methylene Chloride	4-Methyl-2-Pentanone	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
Acrylonitrile	2-Nitropropane	1,2,3-Trichloropropane	1,3,5 Trichlorobenzene
trans-1,2-Dichloroethene	Toluene	2-Chlorotoluene	
Methyl-t-Butyl Ether	trans-1,3-Dichloropropene	4-Chlorotoluene	Bromofluorobenzene (SS)
t-Butyl Alcohol	Ethyl Methacrylate	n-Propylbenzene	1,2-Dichlorobenzene-d4 (SS)
1,1-Dichloroethane	1,1,2-Trichloroethane	1,3,5-Trimethylbenzene	
2,2-Dichloropropane	Tetrachloroethene		
cis-1,2-Dichloroethene	1,3-Dichloropropane		
2-Butanone	2-Hexanone		
Propionitrile	trans-1,4-Dichloro-2-butene		
Methyl Acrylate	Pentachloroethane		
Bromochloromethane	Hexachloroethane		
Methacrylonitrile	Nitrobenzene		
Tetrahydrofuran			
Chloroform	1,2-Dichloroethane-d4 (SS)		
1,1,1-Trichloroethane	Toluene-d8 (SS)		
1-Chlorobutane			

Table 5: QC Frequency, Criteria and Recommended Corrective Action (EPA 524.2)

QC Check	Acronym	Minimum Frequency	Acceptance Criteria	Corrective Action
Tune Standard	BFB	Prior to Initial Calibration and every 12 hours	See Table	Correct problem and reanalyze
Initial Calibration	ICAL	Initially and when BFB or CCV fails	RSD ≤ 20%	Correct problem and repeat calibration
Quality Control Sample	QCS** (ICV)	After each calibration, prior to sample analysis.	± 30 % of expected value	Correct problem, verify second source standard. If that fails, repeat calibration.
Continuing Calibration Verification	CCV	After each Tune Standard	RF ± 30% *internal standards and surrogates	Correct problem, reanalyze CCV. If that fails, repeat calibration and reanalyze all samples since last successful calibration.
Laboratory Reagent Blank	LRB (MB)	One per batch of 20 samples or less	No analytes ≥RL	Correct problem, and reanalyze MB and associated samples.
Laboratory Fortified Blank	LFB** (LCS)	One per batch of 20 samples or less. See	± 30 % of expected value	Correct problem, and reanalyze LCS, MB and associated samples for failed analytes if sufficient sample volume is available.
Laboratory Fortified Matrix	LFM (MS)	10% or one per batch, whichever is more frequent.	± 30 % of expected value	Examine project DQO's with Project Manager. Evaluate data to determine if outage is related to analytical error or matrix effect. Qualify results with an appropriate data qualifier.
Sample Duplicate	LD1/LD2	2 per analytical batch	RPD ≤ 20%	Examine project DQO's with Project Manager. Evaluate data to determine source of difference between results Qualify results with an appropriate data qualifier.
Field Reagent Blanks	FRB (Trip Blank)	1 per sample set	No analytes ≥RL	Investigate source; qualify results; mote in narrative.

** Internal standards and surrogate quantitation ion area must not decrease by more than 30% from the areas measured in the most recent continuing calibration check or by more than 50% from the areas measured during the initial calibration.*

***The LFB is a second source standard analyzed after each calibration to serve as the QCS and with each sample set to serve as the LFB.*

Appendix A: Terms & Definitions
The following definitions were taken from EPA Method 524.2, Revision 4.1, Section 3.0.

Internal Standard (IS): A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogate components of the same sample or solution. The internal standards must be an analyte that is not a sample component.

Surrogate Analyte (SA): A pure analyte(s), which is extremely unlikely to be found in any sample and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance for each sample. The surrogate analyte is also known by the acronym SS.

Laboratory Duplicate (LD1 and LD2): Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of the LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

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

Laboratory Reagent Blank (LRB): An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates 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. The LRB is also known as the Method Blank (MB).

Field Reagent Blank (FRB): An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment. The FRB is also known as the Trip Blank (TB).

Laboratory Performance Check Solution (CCV): An analytical standard containing all target analytes, surrogate and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

Laboratory Fortified Blank (LFB): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes, from a source independent from the calibration standards, are added in the laboratory. The LFB 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. The LFB is also known as the Laboratory Control Sample (LCS).

Laboratory Fortified Sample Matrix (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed

exactly like a sample and its purpose is to determine whether sample matrix contributes bias to the analytical results. The LFM is also known as the Matrix Spike (MS).

Stock Standard Solution: A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

Primary Dilution Standard Solution: A solution of several analytes prepared in the laboratory from stock standard solutions and diluted in an appropriate solvent as needed to prepare calibration solutions and other needed analyte solutions.

Calibration Standard (CAL): A solution prepared, in VOC free reagent water, from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

Quality Control Sample (QCS): An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The QCS is obtained from a source external to the laboratory and different from the source of the calibration standards. It is used to check the laboratory's performance with externally prepared test materials.

STANDARD OPERATING PROCEDURE
STL BURLINGTON

EPA 350.2 AMMONIA-NITROGEN
Applicable Matrices: Non-Potable Water, Solid and Chemical Materials

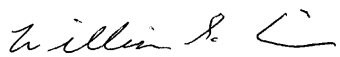
APPROVAL SIGNATURES

Deborah A. Loring
Laboratory Director

Date: November 6, 2006

Kirstin L. McCracken
Quality Assurance Manager

Date: November 6, 2006



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Date: November 6, 2006

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of Ammonia as Nitrogen (Ammonia as N) in non-potable water and solids.

1.2 The routine reporting limit (RL) for water is 0.10 mg/L and 5.0 mg/kg for solids.

2.0 SUMMARY OF METHOD

2.1 Samples submitted for analysis are buffered at a pH of 9.5 with a borate buffer in order to decrease hydrolysis of cyanates and organic nitrogen compounds and then distilled into a solution of boric acid. The ammonia in the distillate is then determined colorimetrically by nesslerization.

2.2 This procedure is based on EPA Method 350.2, Nitrogen, Ammonia (Colorimetric, Titrimetic, Potentiometric Distillation Procedure), Editorial Revision 1974.

3.0 DEFINITIONS

3.1 Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1 A number of aromatic and aliphatic amines, as well as other compounds, both organic and inorganic, will cause turbidity upon the addition of the Nessler reagent, so distillation to eliminate these is required.

4.2 Samples are pretreated with sodium thiosulfate before distillation to remove residual chlorine.

5.0 SAFETY

5.1 Employees must be trained on and they must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Safety Concerns

There are no special safety concerns associated with this method.

5.3 Primary Materials Used

Table 1 in Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all

materials used in the procedure**.** A complete list of materials used can be found in section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Analytical Balance: capable of accurately measurement to 0.01 g.

6.2 Volumetric Flasks, Class A: 10, 50, 100, 500 & 1000 mL sizes. Wash all glassware after use with 10% HCl solution and rinse thoroughly with reagent water.

6.3 Spectrophotometer for use at 425 nm with a 2 cm cuvette.

6.4 Distillation System: WestCo "Easy-Dist" distillation system w/100 mL distillation flasks; 20 position or equivalent.

6.5 Pipettes: 1.0 & 5.0 mL sizes, Finpipette or equivalent.

6.6 Graduated Cylinders; 50 & 500 mL sizes.

6.7 Narrow Range pH paper.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Ammonium Chloride (NH_4Cl): Reagent grade; J.T. Baker or equivalent

Concentrated Sulfuric Acid (H_2SO_4):Reagent grade; J.T. Baker or equivalent

Sodium Borate ($Na_2B_4O_7$ - $10H_2O$): Reagent grade; J.T. Baker or equivalent

Boric Acid: Reagent grade (H_3BO_3): J.T. Baker or equivalent

Nessler Reagent: Thomas Scientific or equivalent. The reagent should exhibit a pale yellow color. Do not use if the reagent is cloudy, is orange in color, or has a noticeable orange precipitate.

Sodium Thiosulfate ($Na_2S_2O_3$ $5H_2O$): Reagent Grade, J.T. Baker or equivalent

Sodium Hydroxide (NaOH): Reagent Grade, J.T. Baker or equivalent

Borate Buffer: Measure 179.55 g sodium borate into a 5-gallon plastic carboy and adjust to volume with reagent water. Adjust the pH of the solution to pH 9-10 using saturated NaOH. Assign an expiration date of six months and store at room temperature.

Boric Acid Solution: Measure 76 g boric acid into a one-gallon plastic container and adjust to volume with reagent water. Assign an expiration date of six months and store at room temperature.

Sodium Thiosulfate, 1/70N: Measure 3.5 g $Na_2S_2O_3$ $5H_2O$ into a 1L volumetric flask and adjust to volume with reagent water. Assign an expiration date of six months and keep refrigerated.

Sodium Hydroxide Solution, Saturated: Add ~500 mL of reagent water to a 1L volumetric flask. Add 1000 g NaOH pellets and mix to dissolve. Dilute the solution to volume with reagent water. Assign an expiration date of six months and store at room temperature.

Sulfuric Acid, 1N: Add 300 mL of reagent water to a 1L volumetric flask. Slowly add 28 mL of concentrated sulfuric acid to the flask then dilute to volume with reagent water. Assign an expiration date of six months and store at room temperature.

7.2 Standards

Unless otherwise specified assign an expiration date of six months from date of preparation unless the expiration date of the parent standard solution expires sooner, in which case use the earliest expiration date. Store all standards and reagents in the refrigerator at a temperature of 2-6^{o}C.

Primary Source Ammonia as N Stock Standard, 1000 mg/L: Measure 3.819g of ammonium chloride into a 1L volumetric flask that contains ~ 500 mL of reagent water. Add three drops of concentrated sulfuric to preserve and adjust to volume with reagent water. Assign an expiration date of six months and store refrigerated.

Ammonia as N Working Standard, 2 mg/L: Measure 2 mL of 1000 mg/L Ammonia as N stock into a 1L volumetric flask that contains ~ 500 mL of reagent water. Add three drops of concentrated sulfuric to preserve and adjust to volume with reagent water. Assign an expiration date of six months and store refrigerated.

Second Source Ammonia as N Stock Standard, 1000 mg/L, SCP Science or equivalent.

Second Source Ammonia as N ICV Working Standard, 50 mg/L: Measure 5 mL of the 1000 mg/L second source Ammonia as N Stock Standard into a 100 mL volumetric flask that contains ~ 50 mL of reagent water. Add three drops of concentrated sulfuric to preserve and adjust to volume with reagent water. Assign an expiration date of six months and store refrigerated.

8.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1 For waters, collect a minimum sample volume of 100 mL in plastic or glass containers and that contain sufficient sulfuric acid to preserve the sample to a pH <2. For soils, collect a minimum sample size of 50 g in plastic or glass containers. Immediately following collection ice all samples to 4°C (±2˚C) and maintain the samples at that temperature until sample preparation and analysis.

8.2 The holding time for water and soils samples is 28 days from date of collection.

8.3 Unless otherwise specified by client or regulatory program, following analysis, samples are retained for a minimum of 30 days after date of submission of the data report and then disposed of in accordance with all applicable regulations.

9.0 QUALITY CONTROL

9.1 The following QC samples are analyzed with each batch of 20 or less samples: Method Blank (MB), and two Laboratory Control Sample (LCS) of varying concentration. A Matrix Spike (MS) and Sample Duplicate (DP) are prepared with each sample batch when sufficient sample volume is available. Client specific MS/MSD and sample duplicates are performed per client request. The initial calibration curve is checked with a second source Initial Calibration Verification standard (ICV), Continuing Calibration Verification standards (CCV), and Continuing Calibration Blanks (CCB). The minimum frequency requirements, acceptance criteria and recommended corrective action for all QC samples are summarized in Table 2, Section 18.0.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Initial Calibration

Using the 2 mg/L Ammonia as N Working Standard (7.1.3), prepare the following calibration standards in 50 mL volumetric flasks:

Curve Standard	2mg/L Standard (mL)	Reagent Water (mL)	Final Volume (mL)	Final Concentration (mg/L)
Blank	0	50.0	50	0.000
Level 1	2.5	47.5	50	0.100
Level 2	5.0	45.0	50	0.200
Level 3	10.0	40.0	50	0.400
Level 4	15.0	35.0	50	0.600
Level 5	20.0	30.0	50	0.800
Level 6	30.0	20.0	50	1.20
Level 7	40.0	10.0	50	1.60
Level 8	50.0	0	50	2.00

Add 2 mL of Nessler reagent to each curve standard and allow the color to develop for 15 minutes. Read the absorbance of each calibration level using the spectrophotometer at 425 nm. See Section 11.4 for the analysis procedure.

Prepare a calibration curve by plotting the absorbance values of the calibration standards against their known concentrations using a linear regression analysis. The correlation coefficient must be $\geq$ 0.995 for the calibration to be considered acceptable. If this criterion is not met, the calibration procedure must be repeated before sample analysis.

10.2 Initial Calibration Verification (ICV) – 1.0 mg/L

Immediately following the initial calibration, analyze an ICV. To prepare the ICV standard, measure 2.0 mL of the second source 50 mg/L Ammonia as N ICV Working Standard into a 100 mL volumetric flask and adjust to volume with reagent water. Add 2 mL of Nessler reagent and swirl to mix. Allow 15-20 minutes for color development. Analyze the standard and calculate the concentration of Ammonia as N in mg/L from the calibration curve using linear regression. Calculate the percent recovery. The percent recovery of the ICV must be 90-110%. If it is outside of this range, corrective action may be taken and it may be re-analyzed once. If it is still outside of the range, the calibration procedure must be repeated prior to sample analysis.

10.3 Continuing Calibration Verification (CCV) – 0.60 mg/L and 1.20 mg/L

Analyze CCV standard at the beginning of the run, every 10 samples, and at the end of the run. Vary the CCV concentrations between 0.60 mg/L and 1.20 mg/L alternately through the analytical sequence.

To prepare the 0.60 mg/L CCV, measure 15 mL of the 2 mg/L Ammonia as N Working Standard into a 50 mL volumetric flask and adjust to volume with reagent water. To prepare the 1.2 mg/L CCV, measure 30.0 mL of the 2 mg/L Ammonia as N Working Standard (7.1.3) into a 50 mL volumetric flask, and adjust to volume with reagent water. Add 2 mL of Nessler reagent to each standard and swirl to mix. Allow 15-20 minutes for color development.

Analyze the CCV standards and calculate the concentration of Ammonia as N in mg/L from the calibration curve using linear regression. Calculate the percent recovery. The percent recovery of the CCV must be 90-110%. If this criterion is not met, perform corrective action and repeat analysis of the failing CCV unless the recovery of the CCV is high and ammonia is not found in any field samples in which case, the data is acceptable and corrective action is not required. If the CCV fails after reanalysis, perform additional corrective action then repeat initial calibration. Alternatively, analyze two consecutive CCVs at differing concentrations. If these CCV samples are within acceptance criteria analysis may continue, otherwise initial calibration must be repeated. If the initial calibration must be repeated, re-analyze all bracketed samples (samples run just prior to and just after the failing CCV).

10.4 Continuing Calibration Blanks (CCB)

Analyze a CCB consisting of 50 mL of reagent water immediately after each CCV. To prepare the CCB, add 2 mL of Nessler reagent to a 50 mL flask that contains 50 mL of reagent water. Mix well and allow 15-20 minutes for color development.

For analysis to proceed, the CCBs must not contain Ammonia at greater than the RL. For Department of Defense analyses, Ammonia in the CCB must be < 0.05 mg/L for the analysis to proceed. If however, all resulting analyses are greater than 10 times the blank analysis, the data is acceptable.

11.0 PROCEDURE

11.1 Preliminary Glassware Preparation

After each use, wash the boiling tubes, caps, sloped T joints, 50 mL graduated cylinders, and condensing stems in the dishwasher. Rinse the condensers and test tubes with 10% HCl and then rinse well with reagent water.

Prior to use, inspect glassware for weakness and dirt or film residue. The glassware must be scrupulously cleaned to prevent contamination. If necessary, re-rinse with 10% HCl and reagent water. Rinse the condenser stems with reagent water and ensure that the water runs freely through them, that the stems are not blocked, and that they drain well.

11.2 Water Sample Preparation

Add 5-10 boiling chips to each boiling flask.

Using a graduated cylinder, measure 50 mL of each sample into a 100 mL distillation tube.

Prepare the QC samples as follows:

Method Blank: Measure 50 mL of reagent water into a distillation tube.

LCS#1 0.40 mg/L Ammonia as N: Measure 10.0 mL of the 2.0 mg/L Ammonia as N Working Standard into a 50 mL volumetric flask and adjust to volume with reagent water. Mix well and add to a distillation tube.

LCS#2 0.80 mg/L Ammonia as N: Measure 20.0 mL of the 2.0 mg/L Ammonia as N Working Standard into a 50 mL volumetric flask and adjust to volume with reagent water. Mix well and add to a distillation tube.

Sample Duplicate and 0.80 mg/L Ammonia as N Matrix Spike (MS): Measure additional 50 mL aliquots for each sample duplicate and MS into distillation tubes. To prepare the MS, add 0.5 mL of 1000 mg/L Ammonia as N Stock Standard into a 10 mL volumetric flask and adjust to volume with reagent water. Prepare fresh daily. Add 0.8 mL of the 50

mg/L Ammonia as N Working Standard to the MS aliquot. This preparation is equivalent to a matrix spike concentration of 0.80 mg/L Ammonia as N.

Add 1 mL of (1/70 N) sodium thiosulfate to each field and QC samples to remove any residual chlorine.

Proceed to the distillation procedure described in section 11.4.

11.3 Soil Sample Preparation

Add 5-10 boiling chips that have been pre-soaked in 10 N NaOH to each distillation tube.

Measure ~1.0 g of each sample into a 100 mL distillation tube and add 50 mL of reagent water using a graduated cylinder.

Prepare the QC samples as follows:

Method Blank: Measure ~1.0 g of Teflon chips into a labeled distillation tube and add 50 mL of reagent water using a 50 mL graduated cylinder.

LCS#1 20 mg/kg Ammonia as N: Measure approximately 1.0 g of Teflon chips into a labeled distillation tube. Measure 10.0 mL of the 2.0 mg/L Ammonia as N Working Standard into a 50 mL volumetric flask and adjust to volume with reagent water. Mix well and add to a distillation tube. This is equivalent to 0.40 mg/L in solution and 20 mg/kg in the final distillate.

LCS#2 40 mg/kg Ammonia as N: Measure approximately 1.0 g of Teflon chips into a labeled distillation tube. Measure 20.0 mL of the 2.0 mg/L Ammonia as N Working Standard into a 50 mL volumetric flask and adjust to volume with reagent water. Mix well and add to a distillation tube. This is equivalent to 0.80 mg/L in solution and 40 mg/kg in the final sample.

Sample Duplicate and 80 mg/kg Ammonia as N Matrix Spike (MS): Measure additional 1.0 g aliquots for a sample duplicate and each MS into 100 mL distillation tubes and add 50 mL of reagent water using a graduated cylinder. To prepare the MS, measure 0.5 mL of 1000 mg/L Ammonia as N Stock Standard into a 10 mL volumetric flask and adjusting to volume with reagent water. Prepare fresh daily. Add 0.8 mL of the 50 mg/L Ammonia as N Working Standard to the MS aliquot. This is equivalent to an MS concentration in solution of 0.80 mg/L Ammonia as N, and 80 mg/kg Ammonia as N in sample.

Add 1 mL of (1/70 N) sodium thiosulfate to each field and QC sample to remove any residual chlorine.

Proceed to the distillation procedure described in section 11.4.

11.4 Distillation Procedure

Add 5 mL of boric acid to each graduated cylinder that is to be used for distillate collection.

Assemble the glassware in the micro-distillation unit. Take care to ensure that all connections are tight and the clips are used where appropriate. Ensure that all joints are seated and that the condenser stem tips are submerged in the boric acid solution, but that they do not touch the bottom of the collection tube. If necessary, place cardboard shims under the collection tubes to ensure submersion.

Turn on the condensers, and check the water flow using the clear loop attached to the chilled water loop. The water flow should create approximately 1 revolution of the red indicator ball per second. Let the chilled water loop run for approximately 5-10 minutes before turning on the distillation heating program to ensure that the condensers are cool.

To each sample, including QC samples, add 10N NaOH drop-wise to a pH of 9.5, using narrow range pH paper to check the sample pH then add 5.0 mL of borate buffer to each sample.

To begin the distillation, turn on the Easy-Dist keypad. The temperature program is pre-set as follows: Ramp 10^{o}C per minute to 190^{o}C, 0.4 hour hold, then 1^{o}C per minute to 210^{o}C, 0.5 hour hold. Press “start” to begin the distillation process.

Observe the samples as they begin to boil. The samples may “pop”; if this occurs, more boiling chips may be needed. If the distillation stems in the collection tubes fill up, quickly remove the cap on the slope-T to allow draining of stems and replace caps immediately. Take care during this step, as hot steam will be released. Watch for condensate on the outside of the condensers, and wipe when needed to prevent condensate from dripping into the collection tubes. Samples should distill in approximately 45 minutes – 1 hour.

Some samples will distill more quickly than others so it is important to monitor the distillation and stop at the appropriate time. Monitor each distiller set up and remove the collection tube when between 30 and 35 mL of distillate has been collected. Note: this is in addition to the 5 mL of Boric Acid already in the collection tube, so the goal is to collect a total volume, including Boric Acid, of between 35 and 40 mL. Note that a certain volume collects in the distillation stem, and this will drain when the distillation is stopped. Therefore, try not to distill more than 40 mL as this will elevate the final reporting limit. If more than 50 mL of total distillate is collected, make sure to note this in the Ammonia logbook.

To stop an individual distillation: using heat resistant gloves, release the cap from the slope-T joint and lift the boiling flask, making sure that the condensing stems are still submerged. The graduated cylinder may then be removed.

Once all samples have reached the final volume, turn off the heat and the chilled water loop and disconnect the condensers. If the condensers are not disconnected the boiling tubes could break.

Adjust the distillate volume in each graduated cylinder to 50 mL with reagent water.

11.5 Colorization Procedure

Transfer 10 mL of each sample distillate to a unique reaction vessel. Add 0.4 mL of Nessler reagent. Mix well and allow 15 minutes for color development.

11.6 Spectrophotometer Analysis

Turn the spectrophotometer on and set it to absorbance. Adjust the wavelength to 425 nm. Then let the spectrophotometer warm up for 15 minutes.

A 2 cm cuvette is used for analysis. When using the cuvette, ensure it is clean, has no scratches on the glass, and no fingerprints. Fill it with nanopure water and press the 100% T button. The spectrophotometer is then zeroed.

For each new run, calibrate the spectrophotometer with a CCV and CCB as outlined in Section 10.3-10.4.

For each reading, fill the 2 cm cuvette and read the % absorbance (%A) at 425 nm. Record the %A in the Ammonia logbook.

Between runs, dump the sample/standard in the cuvette and rinse well with reagent water. Wipe the outside with a Kimwipe if any droplets of sample, fingerprints, or smudges get on the outside walls of the cuvette.

An example analytical sequence is given below:
CCV
CCB
Method Blank
LCS#1
LCS#2
10 samples
CCV
CCB
10 samples
CCV
CCB

Calculate the concentration of Ammonia as N in mg/L in each sample by entering the absorbance readings, dilution factor, sample volume/mass and percent solids for each sample ID into the document controlled EXCEL spreadsheet created for this purpose.

The concentration of the target analyte is then determined from the entered values using linear regression analysis using the linear regression equation generated in the initial calibration (10.1). Samples with concentrations that exceed the linear range must be diluted with reagent water and the colorization step repeated. Adjust the results for solid

samples for % solids and reported on a dry weight basis.

12.0 CALCULATIONS

12.1 Aqueous Sample Concentration

$$\text{mg/L Ammonia as N} = \frac{\text{mg/L Ammonia as N}_{\text{distillate}} \times \text{Distillate Volume (mL)}}{\text{Sample Volume (mL)}}$$

12.2 Solid Sample Concentration

$$\text{mg/kg Ammonia as N (As Received)} = \frac{\text{mg/L Ammonia as N}_{\text{distillate}} \times \text{Distillate Volume (mL)}}{\text{Sample Volume (g)}}$$

$$\text{mg/kg Ammonia as N (Dry Weight)} = \frac{\text{mg/L Ammonia as N}_{\text{distillate}} \times \text{Distillate Volume (mL)}}{\text{Sample Volume (g)} \times \text{Percent Solids}}$$

12.3 Percent Recovery (%R) (ICV, LCS, CCV)

$$\%R = \frac{SR}{SA} \times 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

12.4 Percent Recovery (%R) MS

$$\text{MS Recovery(\%)} = \frac{SSR - SR}{SA} \times 100\%$$

Where:
SR= Sample Result
SSR= Matrix Spike Result
SA=Concentration of Spike Added

12.5 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:
D1 = Sample result
D2 = Matrix duplicate result

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

Primary review of the data is performed by the analyst(s) that performed the procedure and secondary review is performed by a senior analyst or a data review analyst to ensure that samples, standards and QC samples meet performance criteria given in Table 1, Section 18.0. If the results do not fall within the established limits or criteria, corrective action should be performed. If corrective action is not taken or unsuccessful, the situation should be reported in the project narrative. All data that does not meet established criteria must be flagged with the appropriate data qualifier(s).

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 A Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the laboratory SOP for MDL determination.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2 Waste streams produced

The following waste streams are produced when this method is carried out.

- Caustic waste – 2.5 L glass satellite container.

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations, The procedures for waste management are further given in the laboratory SOP LP-LB-0010 *Hazardous Waste.*

16.0 REVISION HISTORY

16.1 Title Page: Changed to reflect current management team.

16.2 Section 6.0: removed recommendation to use AMK glassware for distillation.

16.3 Section 6.0: AMK glassware added as recommended glassware.

16.4 Section 6.7: changed pH paper specified for use as narrow range instead of wide.

16.5 Section 7.0: Changed Standard Preparation to include addition of Sulfuric acid before adjusting to final volumes. Changed LCS and LLS source to same standard as curve source. Changed Normality of Sodium Hydroxide used to adjust sample pH. Corrected error from pH 7 to 9.5.

16.6 Section 7.1: added detail; expiration date and storage conditions to reagents.

16.7 Section 10.1: revised calibration points; starting calibration at 0.10 mg/L and added a 0.60 mg/L. Changed transmittance to absorbance.

16.8 Section 11.0: Changed procedure for adjusting pH of sample from using phenolphthalein to pH paper. Changed the length and operating conditions of micro-distillation procedure and added detail. Corrected spectrophotometer readings from transmittance to absorbance.

16.9 Section 15.0: Added caustic waste as a waste stream.

16.10 Section 18.0, Table 2.0: Widened ICV/CCV criteria to 85-115% and QC outage errors corrected, additional corrective action direction provided.

16.11 Entire document: Removed reference to, and procedures for, macro distillation and low level calibration check standard.

16.12 Entire Document: Added Ammonia as N to clarify that standard concentrations and final reporting are expressed as Nitrogen rather than ammonia

17.0 REFERENCES

17.1 EPA Method 350.2, Nitrogen, Ammonia (Colorimetric, Titrimetic, Potentiometric Distillation Procedure), Editorial Revision 1974.

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Primary Materials Used, Exposure Limits and Hazards
18.2 Table 2: QC Summary and Recommended Corrective Action
18.3 Appendix A: Terms & Definitions

Table 1: Primary Materials Used

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Ammonia	Corrosive Poison	50 ppm-TWA	Vapors and mists cause irritation to the respiratory tract. Causes irritation and burns to the skin and eyes
Sodium Hydroxide	Corrosive	2 mg/m3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 mg/m3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary and Recommended Corrective Action

QC Sample	Frequency	Acceptance Limits	Corrective Action
ICAL	As needed, as indicated by LCS and CCVs.	r ≥ 0.995	Check standards, re-calibrate
Initial Calibration Verification (ICV)	After initial calibration.	%Recovery 85-115%	Check formulation of standards and ICV, re-prepare standards and/or ICV and re-analyze associated samples if required
Method Blank (MB)	1 per batch of 20 samples or less.	< RL ½ RL (DoD) unless samples are all greater than 10 times blank level	Re-analyze: if still above RL, re-prepare and re-analyze batch. Report data if samples > 10 times blank level.
Continuing Calibration Verification (CCV). Note: CCV concentrations are varied throughout the analytical sequence.	Every ten (10) samples and at the beginning and end of analysis	%Recovery 85-115%	Take corrective action, re-analyze once, if still outside limits, further corrective action may be taken, however, two consecutive passing CCVs must pass in order for the analysis to proceed, or an initial calibration curve must be performed. Report data if CCV high and all sample results Not Detected.
Continuing Calibration Blank (CCB)	After CCV	< RL ½ RL (DoD)	Re-analyze once, if still outside limits, check reagents, glassware, and instrument for possible contamination and/or drift. Re-analyze previous 10 samples. Report data if samples > 10 times blank level.
Laboratory Control Sample (LCS #1)	1 per batch of 20 samples	85-115%	Re-analyze: if still outside limits, re-prepare and re-analyze batch. If samples are Not Detected and LCS high, report data.
Laboratory Control Sample (LCS #2)	1 per batch of 20 samples	85-115%	Re-analyze: if still outside limits, re-prepare and re-analyze batch. If samples are Not Detected and LCS high, report data.
Method Blank (MB)	1 per batch of 20 samples	< RL ½ RL (DoD)	Re-analyze: if still above RL, re-prepare and re-analyze batch. Report data if samples > 10 times blank level.
Matrix Duplicate (DP)	1 per batch of 20 samples	RPD ≤ 20	The DP is used to assess the effect of the sample matrix on the precision of the method. Evaluate any DP outside limits and note a non-conformance if a matrix effect is indicated.
Matrix Spike (MS)	1 per batch of 20 samples	85-115%	The MS is used to assess the effect of the sample matrix on the accuracy of the method. Evaluate any MS outside limits and note a non-conformance if a matrix effect is indicated.

Appendix A: Terms & Definitions

Accuracy: the degree of agreement between a measurement and the true or expected value, or between the average of a number of measurements and the true or expected value.

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration: the establishment of an analytical curve based on the absorbance, emission intensity or other measured characteristic of known standard.

Calibration Blank (ICB/CCB): a volume of reagent water acidified with the same acid matrix as in the calibration standards.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Calibration Standards: a series of known standard solutions used to calibrate the instrument response with respect to analyte concentration.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time. Usually from the same source as the calibration curve.

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

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix: the substrate of a test sample.

Matrix Duplicate (MD): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Percent Solids (%S): the proportion of solid in a soil sample.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Quality Control Sample: a control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

STANDARD OPERATING PROCEDURE
STL BURLINGTON

EPA 365.2 TOTAL PHOSPHORUS AS P
Applicable Matrices: Non-Potable Water, Solid and Chemical Materials

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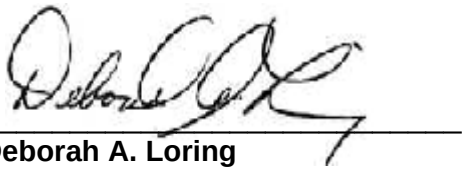
APPROVAL SIGNATURES

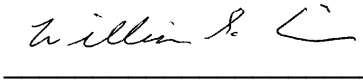


Deborah A. Loring
Laboratory Director

Date: November 6, 2006

Kirstin L. McCracken
Quality Assurance Manager

Date: November 6, 2006



William S. Cicero
Department Manager

Date: November 6, 2006

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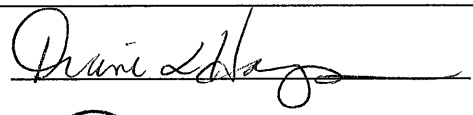
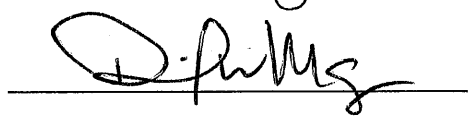
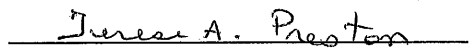
TITLE: Wet Chemistry
Inorganic Ions by Ion Chromatography

Updated by:	Signature:	Date:
Carla Bonner Supervisor, Wet Chemistry		3/2/07

Approved by:	Signature:	Date:
Diane L. Harper Inorganics Manager		3-1-07
David W. Mazur Env. Health & Safety Coor.		3/1/07
Terese A. Preston Quality Manager		3/2/07

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Full Signature Approvals Are Kept on File
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1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) defines the procedure for determining the following inorganic anions by Ion Chromatography: Fluoride, Chloride, Nitrite-N, Bromide, Nitrate-N, Ortho-Phosphate-P, and Sulfate. This SOP was written using EPA Method 300.0 and SW-846, 3rd Edition, Method 9056 as references.

On occasion, clients request slight modifications to this SOP. These modifications are addressed on a case-by-case basis with the range of accuracy (i.e., MDLs, linearity check or PT sample) verified prior to implementation. Any modifications would be written into a Quality Assurance Plan (QAP), authorized via laboratory signature approval, and mentioned in the data package's case narrative.

Specific requirements pertaining to the DOD Version 3.0 are located in Appendix A. These requirements are additionally applicable to all NFESC projects. Any deviations from these procedures and/or variances from, must be addressed appropriately in accordance with standard operating protocol and pre-approved on a project-by-project basis.

1.1 Method Sensitivity

NOTE: Results of linear range and MDL studies indicate the need for changes in calibration standard concentrations; ICV/LCS concentrations; and reporting limits.

1.1.1 Method Detection Limits / Linear Range Verification

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified every 6 months. Attachment 1 (Standards/QC Summary Table) defines the preparation and concentrations of the IDL / MDL standards. The upper end of the calibration curve must be verified every 6 months by running an alternate source standard at the concentration of the highest standard. This is called the Linear Range Standard (LRS) and must be within 5% of the known concentration.

1.1.2 Instrument Detection Limits

Instrument Detection Limits (IDLs) are generated every 6 months. The MDLs are performed at the same frequency and same concentration. As current IDL's do not require true sample preparation, the two are equivalent and used interchangeably.

1.1.3 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error; values specified by the EPA methods; or other project and client requirements. Reporting limits are maintained at values ~3-5x the respective MDL to ensure confidence in the value reported. Refer to Attachment 1 for the laboratory's reporting limits.

NOTE: Reporting limits will vary depending on sample size; dilutions associated with matrix interference or exceedence of the linear concentration range; and dry weight reporting.

1.2 Definitions

Refer to Section 3.0 of the Laboratory's Quality Manual (LQM).

1.3 Summary of Method

A small volume of sample, typically 2-3 mLs, is introduced into an ion chromatograph (IC). The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and a conductivity detector. For solids, the analysis is preceded by an extraction procedure.

2.0 INTERFERENCES

- Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems.
- Possible interference from the water dip or negative peak that elutes near the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent to 100 mLs of each standard and sample.
- Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.
- The quantitation of un-retained peaks should be avoided. Low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and co-elute with or near the fluoride peak would bias the fluoride quantitation in some drinking and most waste waters.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

3.1 Specific Safety Concerns or Requirements

- Potassium Nitrate and Sodium Nitrate are strong oxidizers; therefore, do not store them near any combustible materials. These chemical are stable under prescribed conditions of use and storage (i.e., store protected from air). Note: These chemicals are not routinely use at STL Chicago for IC analysis. They may be used in the event a purchased stock standard becomes unusable and the analyst must prepare a stock locally. They are kept in inventory.
- Sodium Fluoride is highly toxic. Note: It is not routinely used at STL Chicago, but may be, in the event a fluoride stock must be prepared locally. It is kept in inventory.
- Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, upon occasion, caused a filter disc to burst during the process.

3.2 Primary Materials Used

Because STL Chicago purchases 1000 mg/L stock standards for IC analysis, the hazardous salts in the table below are not used except in the event that local preparation of a stock becomes necessary.

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Nitrate	Oxidizer	None	Causes irritation to the respiratory tract, skin and eyes. Symptoms may include coughing, shortness of breath. Symptoms include redness, itching, and pain.
Sodium Fluoride	Poison	2.5 Mg/M3-TWA as F	**Highly Toxic.** Causes severe irritation to the respiratory tract, symptoms may include coughing, sore throat, and labored breathing. Causes irritation, with redness and pain. Solutions are corrosive. Eye irritant! May cause irritation and serious eye damage. Effects may not appear immediately.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.

1 – Always add acid to water to prevent violent reactions.
2 – Exposure limit refers to the OSHA regulatory exposure limit.

4.0 EQUIPMENT AND SUPPLIES

- Dionex DX-120 Ion Chromatograph
- Dionex DX-100 Ion Chromatograph
- Ionpac AG14A-5 um (3 X 30 mm) Guard Column
- Ionpac AS14A-5 um (3 X 150 mm) Analytical Column
- ASRS Ultra-4 mm Suppressor
- DX LAN Card for DX-120
- Dionex Advanced Computer Interface
- PC equipped with PeakNet software, Release 5.1
- Dionex Automated Sampler
- Vials with or without filter caps for Automated Sampler
- 100 mL volumetric flasks
- High Purity Helium Gas or Nitrogen Gas set to deliver 90-120 psi.
- Eluent reservoirs
- OnGuard II H_{TM} pre-treatment cartridges
- 5 or 10 mL syringes
- 0.45 um syringe filters

5.0 REAGENTS AND STANDARDS

5.1 Eluent, 100x Concentrate

On a balance capable of reading to 0.1 mg, weigh out 84.8 grams of Sodium Carbonate and 8.4 grams Sodium Bicarbonate. Dissolve both in a 1-L class A volumetric flask filled with ~700 mLs Milli-Q water. Dilute to volume.

- Life of Reagent: 6-Months
- Storage Requirements: None

5.2 Eluent Working Solution (8.0 mM Na_2CO_3 / 1.0 mM $NaHCO_3$)

Pipet 10 mLs of the Eluent Stock Solution into a 1-L volumetric flask filled with ~700 mLs of Milli-Q water. Dilute to volume.

- Life of Reagent: 6-Months
- Storage Requirements: None

5.3 Anion Stock Standards

Stock standards are purchased from a vendor (received with the certified values and applying the manufacturer's expiration date). The calibration curve is prepared from Stock Standard I; the ICV/CCV, LCS and MSs are prepared from Stock Standard II.

5.3.1 Purchased Stock Standards (1,000 mg/L)

IC Fluoride Stock I	**WSTICF1**
IC Chloride Stock I	**WSTICC1**
IC Nitrate Stock I	**WSTIC31**
IC Bromide Stock I	**WSTICB1**
IC Nitrite Stock I	**WSTIC21**
IC O-Phos Stock I	**WSTICP1**
IC Sulfate Stock I	**WSTICS1**
IC Chloride Stock II	**WSTICC2**
IC Fluoride Stock II	**WSTICF2**
IC Sulfate Stock II	**WSTICS2**
IC Nitrate Stock II	**WSTIC32**
IC Bromide Stock II	**WSTICB2**
IC Nitrite Stock II	**WSTIC22**
IC O-Phos Stock II	**WSTICP2**

*The Stock II solutions are from an alternate source than the Stock I solutions.

- Life of Standard: 1-Year or manufacturer's recommendation, whichever is less.
- Storage Requirements: Refrigerate at 4 ± 2°C

5.3.2 Calibration Curve

Refer to Attachment 1 for concentrations and preparation.

5.3.3 Initial Calibration Verification (ICV)
Laboratory Control Sample (LCS)
Matrix Spike (MS) / Matrix Spike Duplicate (MSD)

Refer to Attachment 1 for concentrations and preparation.

MS/MSDs will most likely need to be done on multiple sample dilutions. Calculate and report spikes on the same dilution from which the original sample is reported.

5.3.4 Continuing Calibration Verification (CCV)

Refer to Attachment 1 for concentrations and preparation.

6.0 CALIBRATION (NON-DAILY)

The calibration curve is prepared and run monthly or whenever a significant change in instrument response is observed. Some examples of the need for recalibration may include low recovery or concentration of the ICV standard, significant changes in retention times of the anions, or instrument maintenance, which may affect the chromatography. Some sample matrices will affect the retention times of subsequent injections. The calibration is checked immediately after the curve is run and daily with the initial run of an ICV with the requirement of ±10% acceptance criteria. (Refer to Section 7.4) (Refer to the STL Corporate Policy, P-T-001, *Selection of Calibration Points* for further guidance.)

No blank is run as part of the curve, but each curve consists of 6 mixed standards, each of which contains a given concentration of each of the seven anions.

Running a curve over-writes the previous curve, and all subsequent analyses will be processed against the new curve. The Dionex ICs integrate peak areas. Refer to the PeakNet software manual for specifics.

6.1 Retention Times (RTs)

RTs may vary according to ionic size, ionic charge, ion concentration, column type, and ionic composition of the mobile phase. The RT window will be routinely determined using ±5% of the RT for each analyte contained in the Initial Calibration Verification (ICV) standard. Attachment 5 defines an example table that will be used for the calculation of the RT windows and will be included by the analyst with the raw data.

DoD requires that the retention time be established as 3X the standard deviation for each analyte over a 24-hour period. STL Chicago does not have sufficient points in a 24-hour period, but will determine the standard deviation over a period of several days and calculate the retention time window. If the +/-5% window is narrower, STL Chicago will continue to use that method, but will keep the other data on file.

Analyst discretion may be used for RT shifts resulting from complex sample matrices. The instrument must be recalibrated or obtain section manager or QA approval if the RT drifts outside this window. RTs may vary with the use of different columns, assuming that the concentrations of these ions are within ranges of the curves.

7.0 PROCEDURE

7.1 Quality Control Checks, non calibration

Quality Controls	Frequency [1]	Default Control Limits [1,2]
Method Blank (MB)	1 in 20 samples	< Reporting Limit
LCS [3]	1 in 20 samples	Statistical, QAPP, or method limits; whichever is applicable
MS / MSD [4]	[5]	75 - 125% (9056A) 80-120% (300.0)
Matrix Duplicate (MD) [6]	See above	≤ 20 RPD

[1] Client-specific QAPPs may include QC limits and frequency requirements that supersede those given above. Certain client QAPPs may require additional QC types, such as an MRL or DLCK to be run in sequence.
[2] Statistical control limits are available for those clients or projects that require the use of statistical limits. Method 9056 requires 80-120% limits; EPA 300.0 requires 90-110%.
[3] LCS Duplicate (LCSD) is performed only when insufficient sample is available for the MS/MSD or when requested by the client/project/contract.
[4] The sample selection for the MS/MSD is rotated among client samples so that various matrix problems may be noted and/or addressed.
[5] EPA Method 300.0 requires MS's at a 10% frequency (1 in 10 samples); SW-846 Method 9056 requires MS's at a 5% frequency (1 in 20 samples).
[6] MDs are performed only at the client's request or program requirements. The MS/MSDs are the routinely performed matrix QC indicators.

Note: Drinking water samples are analyzed in sets of 10 with a MS and MD performed on the drinking water matrix. Control limits are ≤ 10 RPD for duplicates and 85 - 115% for matrix spikes. LCS recoveries must be 90 - 110%.

7.2 Sample Preservation and Storage

Samples should be collected in scrupulously clean glass or polyethylene bottles.

Anion	Preservation	Hold Time
Fluoride	Cool 4 ± 2°C	28 Days
Chloride	Cool 4 ± 2°C	28 Days
Nitrite-N	Cool 4 ± 2°C	48 Hours
Bromide	Cool 4 ± 2°C	28 Days
Nitrate-N	Cool 4 ± 2°C	48 Hours
Ortho-Phosphate-P	Cool 4 ± 2°C	48 Hours
Sulfate	Cool 4 ± 2°C	28 Days

7.3 Sample Preparation

7.3.1 Waters

Water samples should be filtered prior to analysis using a 0.45 um membrane type filter if the sample appears to have particulates in it. If transition metals are known or suspected to be present in a sample, it is good practice to put the sample through a Dionex OnGuard II H_{TM} column prior to analysis, since transition metals will corrupt the columns. Use these columns with care and appropriate rinsing.

7.3.2 Soils

Weigh 10 grams of the solid sample into a 125 mL Erlenmeyer flask and add 100 mLs of reagent grade water. Spike at this point if applicable. Mix the solution well using a wrist action shaker for 10 minutes, then filter the slurry solution using a 0.45 u membrane type filter. (It is best to let the slurry solution settle for few hours prior to filtering to allow the particulates to settle. This allows for an easier filtration process. **Never compromise the representative composition of the sample in the original container!** Centrifuging is another pre-filtration option.) Soil extracts may also be treated through OnGuard II H_{TM} columns.

7.4 Calibration / Standardization

Calibration Controls	Sequence	Control Limit
Standards	Monthly, prior to samples	y-int < Reporting Limit
Correlation Coefficient	Of calibration curve	$\geq$ 0.995
Initial Calibration Verification (ICV)	Daily, at initiation of run	90 – 110%
Initial Calibration Blank (ICB)	after ICV	< Reporting Limit
Continuing Calibration Verification (CCV)	every 10 readings	90 – 110%
Continuing Calib. Blank (CCB)	after each CCV	< Reporting Limit

NOTE: If the recovery of the CCV has changed more than 5% within a run, recalibrate for that analyte to comply with SW-846 Method 9056.

7.5 Preventive Maintenance

Instrument maintenance is recorded in the instrument maintenance log (Attachment 2). The following checks are completed as necessary to ensure efficient operation of the instrument.

- Periodically check for leaks or spills within the valve compartments. Isolate and repair any leaks.
- Clean up any spills.
- Rinse any dried eluents or reagents off the system components with DI water.
- Check all air and liquid lines for discoloration or crimping. Relocate pinched lines and replace damaged lines.

- Change eluent reservoir filter and in-line filters as needed.
- Some sample matrices will degrade the IC components over time. Placing one to three vials containing concentrated eluent in the schedule after the final CCB may help to prevent the degradation.
- Clean the columns periodically as needed following the Dionex manual. Be sure to place the guard column after the separator column for this procedure.

7.6 Sample Analysis

Enter the sequence of analysis of samples and standards in the instrument's "Schedule File" that is located at C:\PeakNet\Schedule*Month date year.sch*.

Pour approximately 5 mL of each calibration standard, method blank, LCS, and prepared sample into a labeled autosampler vial. Place the vials in sequence into the 6-place vial holders, then place the holders into the autosampler. Take care to limit the number of holders to 10 if the autosampler will be left unattended. More holders can be added when an equal number of spent holders have been removed. Fill the eluent reservoir with working eluent solution (reagent 5.2). Eluent will need to flow through the system until it is equilibrated or for an hour before starting. Start the run when the instrument's general operating conditions are met (see 7.6.1). Refer to the instrument's operational manual for complete details.

7.6.1 General Operating Conditions

Item	Description
Sample Loop Volume	25 uLs
Analytical Column	Ionpac AS14A 5 um (3 X 150 mm)
Eluent	8.0 mM Na_2CO_3 / 1.0 mM $NaHCO_3$
Eluent Flow Rate	0.5 mL / min
Suppressor	ASRS Ultra 4mm Suppressor
Background Conductivity	~ 22 uS (stable)
System Pressure	1600 – 2000 psi (stable)

7.7 Data Evaluation and Documentation

7.7.1 Data File Processing

At the completion of the run, print the Schedule File and the individual Data Files (chromatograms). Additionally, create a .csv file for the run. Export the .csv file to LIMS, by following the keyboard sequence found in Attachment 6.

7.7.2 Raw Data Evaluation and Documentation

Go through the hard copies of each chromatogram while checking the imported data in the LIMS sample result screen. Circle the peak number for each anion being reported on each chromatogram. To the right of each anion name write the appropriate 2-letter data qualifier explaining why the other anions are not being reported (see Attachment 3). Sign and date each chromatogram as it's evaluated.

If manual integration is advised, be sure to print the chromatogram before and after the corrections, and be sure to document on the hard copy why it was done. Manual integrations must be co-signed by the Wet Chemistry Supervisor, Inorganics Manager or someone from QA. See the corporate SOP on Manual Integration (S-Q-004) and Section 9.4 of this SOP for approved manual integration practices.

Complete a Cover Page for each analysis run (CHI-22-12-084). Documentation on this page includes the LIMS Batch, File ID, Instrument, Calibration Date, Standard Traceability, Calibration Range and Data Qualifiers used in the evaluation of the data. The analyst and reviewer signatures are required on this page. Refer to Attachment 3 for examples of above mentioned forms and an example of the LIMS Forms that serve to report the data and its associated QC in the LIMS system.

The complete raw data package for an IC run includes the Cover Page (Attachment 3), the Schedule File, the Retention Time Table (Attachment 5), and the Sample Analysis Reports from the IC. For Level 4 reports, the calibration curve data must also be included.

7.7.3 Traceability of Standards

Upon receipt or preparation, each chemical salt, solvent, acid, standard, or other reagent is entered into LIMS and is issued a unique ID# based upon the type and sequential order in which the item was prepared or received. Further information entered into the LabNet / LIMS includes the manufacturer, lot # (if applicable), the date received or prepared, the expiration date, volume/weight received; concentration (if applicable); preparation details (if applicable), initials of the recording analyst, and the description of the item (i.e., IC Nitrate Stock Solution – LCS/MS). Once the record is created, a unique label is printed and affixed to the appropriate standard/reagent container.

7.74 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review checklist (Attachment 4). Upon the first 100% review, the review checklist is initialed and dated as reviewed and the batch is set to 1st Level review status. The samples will no longer appear on the analyst's backlog at this point. The package, with its review checklist and any comments is submitted to the Supervisor or peer reviewer for a second review. Once again, the review checklist is initialed and dated by the second reviewer and the batch is set to 2nd Level review status.

The completed data review form remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One MB and one LCS will be included in each batch of samples (refer to Section 7.1). Regardless of the matrix being processed, the MB and LCS will be in an aqueous media. The MB will be examined to determine if contamination is being introduced in the laboratory. The LCS will be examined to determine accuracy of the method and cumulative LCS data will provide precision data.

8.1.2 Accuracy will be measured by the percent recovery (%) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. And, precision will be measured by the cumulative reproducibility of the LCSs.

8.1.3 One MS/MSD (or MS/MD) is performed per matrix per sample batch (refer to Section 7.1), unless otherwise requested. Results must agree within the limits defined in Section 7.1 or within internally-derived statistical limits in order to be considered acceptable.

8.2 Corrective Actions

When an out-of-control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out-of-control situation may be caused by more than one variable. The analysts should seek the assistance of their immediate supervisor or manager, QA personnel, or other experienced staff if they are uncertain of the cause of the out-of-control situation. The analysis must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out-of-control data must never be released without approval of the supervisor, inorganics manager, project manager, QA personnel or the lab manager.

Listed below are steps that MUST be taken when an out of control situation occurs:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on the data review checklist;
- document on the checklist that an in-control has been achieved; and write the appropriate Non-Conformance Memo (NCM) in the batch;
- receive approval (signature) of the Supervisor, Inorganics Manager, QA personnel, Project Manager, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

It may be necessary to forward an NCM to the PM/Client for further action/approval prior to reporting of the data.

The following are suggested actions to specific out of control situations:

QC Standard	Suggested Corrective Actions
Calibration Curve	• reanalyze the standard curve; • prepare a new stock and/or working standards; • check the reagents/solutions and prepare fresh if necessary. • 6-month LRS outside 95-105% recovery requires re-calibration.
ICV	• repeat the ICV to verify proper preparation; • prepare a new ICV from the original stock; • check for instrument base-line drift; • restandardize the instrument with existing standards, reanalyze; • check the reagents/solutions and prepare fresh if necessary; • prepare a new stock and/or working standards and recalibrate.
ICB	• prepare a new ICB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).
LCS	• reanalyze the LCS to verify that an out-of-control situation exists; • determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.) • Note any out-of-control LCSs on the data review checklist.
If an LCS Duplicate (LCD) is required, it must meet the control limits of ≤ 20 RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your section manager for proper corrective action.	

QC Standard	Suggested Corrective Actions
MB	• Reanalyze the MB to verify contamination at a level > Reporting Limit; • Determine the source of contamination and correct the problem; • all samples whose concentration is <10 times the MB level must be reprocessed and reanalyzed; any sample which is >10 times the MB level need not be reanalyzed. However, note the out-of-control MB on the data review checklist and an NCM written.
MD (If Required)	• the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies; • if the reanalysis is within the control limits, the second value is reported; • if the reanalysis is still outside of the control limits, the data must be flagged and noted in an NCM.
MS	• If a single spike is performed and it is outside the acceptance limits, it must be repeated to verify the matrix effect. Generally, an MS and MSD are performed together in the same batch as the original sample analysis. For LabNet to report matrix QC it MUST be reported in the same batch as the original sample analysis. • Report all spikes, whether or not they are in control. • Note out-of-control spikes on the data review checklist and NCMs.
CCV	• repeat the CCV to verify proper preparation; • report non-detect sample results if the CCV bias is high; write and NCM • prepare a new CCV from the original stock; • check for instrument base-line drift; • check the reagents/solutions and prepare fresh if necessary; • recalibrate with a new standard curve and repeat all detected if CCV is biased high)samples since the previous in-control CCV; • never dispose of any samples until you are sure that all QC are within their designated control limits.
CCB	• prepare a new CCB to verify proper preparation; • verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; • determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in-control CCB. (Carry over from a previous analysis or reagent contamination are two common sources); • never dispose of any samples until you are sure that all QC are within their designated control limits. • Report only non-detects and samples >10X the contamination level. Write an NCM

9.0 Data Analysis and Calculations

9.1 Sample Concentrations

9.1.1 Waters mg/L = instrument reading x dilution factor

9.1.2 Soils $\text{mg/kg} = \frac{\text{instr. reading (mg/L) x final vol. (mLs)}}{\text{sample wt. (g)}} \times \text{dilution factor}$

9.2 Accuracy

9.2.1 ICV/CCV and LCS % Recoveries $= \frac{\text{observed concentration}}{\text{actual concentration}} \times 100$

9.2.2 MS % Recovery $= \frac{\text{(spiked sample conc. - original sample conc.)}}{\text{spike concentration}} \times 100$

9.3 Precision

9.3.1 Matrix Dup. and LCD Relative Percent Difference (RPD)

$$\text{RPD} = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value + dup. sample value})/2]} \times 100$$

9.4 Manual Integration Policy

In each case where the file has been edited or manual integrations have been performed, the following guidelines apply:

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.
- Manual integrations shall follow the STL Corporate SOP for manual integrations (#S-Q-004).

Manual integrations are most often performed for the following reasons:

- Assignment of correct peak that was mis-identified by the data system.
- Incomplete auto-integration due to high level of target compound detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

All integrations are reviewed by the analyst. All chromatograms and reports are printed after any integration takes place and are routinely included in the data packages.

Manual integrations may be documented in the narrative if so required, however, references to our Corporate Manual Integration SOP (S-Q-004) will be used for explanations, and any further documentation beyond initials and dates will not be done.

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

10.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Waste from this procedure will enter the "Wastewater" wastestream.
- Single component standards will be turned over to the EHSC or Waste Technician.

11.0 METHOD PERFORMANCE CRITERIA

Refer to Sections 1, 6, 7 and 8.

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Attachment 1: Example: IC Standards / QC Summary Table
Attachment 2: Example: Daily Maintenance Log
Attachment 3: Example: IC Cover Page/Schedule File/LIMS Batch Forms
Attachment 4: Example: Data Review Checklist
Attachment 5: Example: Retention Time Window Summary Table
Attachment 6: Example: Data Export to LIMS: Keystroke Sequence
Attachment 7: DoD QSM Version 3: Appendix DOD-B QC Requirements Summary (Table B-1 and Table B-10)
Attachment 8: Example: Retention time study (3X standard deviation)

Historical File:

Revision 00: 01/07/93
Revision 01: 06/13/96
Revision 02: 09/23/98
Revision 03: 06/25/99
Revision 04: 09/26/00
Revision 05: 07/02/02
Revision 06: 11/30/04
Revision 07: 01/06/06
Revision 08: 03/01/07

Reason for Change; Revision 08:

- Annual Review –
- Add DoD method of determining the retention time window
- Remove requirement to alternate CCV concentrations

U:\QC\SOP\WC\300_0.DOC

Attachment 1.

Example: IC Standards / QC Summary Table

STL Chicago

CHI-22-12-070\J-03/07

IC - Standards / QC Summary Table

								High Range	
Parameter	**Fluoride**	**Chloride**	**NO2**	**Bromide**	**NO3**	**O-PO4**	**Sulfate**	**Chloride**	**Sulfate**
Method	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056	EPA 300.0 SW-846 9056
Report Limit mg/L	0.2	0.2	0.1	0.1	0.1	0.2	0.2	5	5
Report Limit mg/Kg	2.0	2.0	1.0	1.0	1.0	1.0	2.0	50	50

Standard	Curve (mg/L) / (ul volume of Standard I per 100 mLs of DI water in a volumetric flask)								
1	0	0	0	0	0	0	0	0	0
2	0.2 (20uL)	0.2 (20uL)	0.1 (10uL)	0.1 (10uL)	0.1 (10uL)	0.20 (20uL)	0.2 (20uL)	5 (500uL)	5 (500uL)
3	0.4 (40uL)	0.5 (50uL)	0.5 (50uL)	0.5 (50uL)	0.5 (50uL)	0.50 (50uL)	0.5 (50uL)	20 (2mL)	20 (2mL)
4	0.6 (60uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	2.5 (250uL)	50 (5mL)	50 (5mL)
5	1.0 (100uL)	3.0 (300uL)	2.0 (200uL)	2.0 (200uL)	2.0 (200uL)	2.0 (200uL)	5.0 (500uL)	100 (10mL)	100 (10mL)
6	1.5 (150uL)	5.0 (500uL)	3.0 (300uL)	3.0 (300uL)	3.0 (300uL)	3.0 (300uL)	7.5 (750uL)	150 (15mL)	150 (15mL)
7	2.0 (200uL)	7.5 (750uL)	5.0 (500uL)	5.0 (500uL)	4.0 (400uL)	4.0 (400uL)	10 (1000ul)		

QC Solution	Concentration (mg/L) / (ul volume of Standard II per 100 mLs of DI water in a volumetric flask)								
ICV/LCS (+/- 10%)	1 (100uL)	3 (300uL)	2 (200uL)	2 (200uL)	2 (200uL)	2 (200uL)	5 (500uL)	50 (5mL)	50 (5mL)
CCV (+/- 10%)	0.6 (60uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	1.0 (100uL)	2.5 (250uL)	20 (2mL)	20 (2mL)
MDL/IDL Conc.	0.2 (20uL)	0.3 (30uL)	0.1(10uL)	0.1(10uL)	0.1(10uL)	0.2 (20uL)	0.3 (30uL)	NA	NA
MS (75-125%)	1 (100uL)	3 (300uL)	2 (200uL)	2 (200uL)	2 (200uL)	2 (200uL)	5 (500uL)	50 (5mL)	50 (5mL)

Notes:

1. Reporting Limits will vary depending on sample size/volume, dilution factors and dry weight reporting for soils.
2. All Standards and QC Solutions are prepared fresh daily.

Revision: 03/01/07

Attachment 2.

Example: Daily Maintenance Log

STL Chicago
IC-4 Dionex Series DX-120
Maintenance Log

Page No.:_____

Action	Initial/Date	Initial/Date	Initial/Date	Initial/Date	Initial/ Date	Initial/Date	Initial/Date
Date analytical column changed							
Analytical column serial number (record when changed)							
Date guard column changed							
Guard column serial number (record when changed)							
Date Nitrogen Tank changed							
Eluent flow rate (~2 mL/min.)							
Background conductivity (~12-20 uS and stable)							
System pressure (~1600-2000 psi and stable)							

Non-Routine Maintenance/Comments:

Reviewed by:_____ Date:_____

Attachment 3.

IC Cover Page / Schedule File / LIMS Forms
(020-001 to 020-006)

STL Chicago

CHI-22-12-084/N-01/06

Cover Page - Ion Chromatograph

LIMS Batch: _____ **FILE ID:**_____**.csv**

Calibration Date: _____

Instrument: (Circle)	
a. IC4: Dionex Series DX-120	DX120.met
b. IC3: Dionex Series DX-100	DX100.met

Standard Traceability

Note: Working Standards are prepared daily from the noted Stock Solutions.

Test	Calibration Curve Stock ID	LCS (ICV-CCV1)/CCV2 MS Stock ID	LCS mg/L	(ICV-CCV1)/CCV2 mg/L	MS mg/L
Fluoride			1.0	1.0 / 0.6	1.0
Chloride			3.0	3.0 / 1.0	3.0
Nitrite-N			2.0	2.0 / 1.0	2.0
Bromide			2.0	2.0 / 1.0	2.0
Nitrate-N			2.0	2.0 / 1.0	2.0
O-PO4			2.0	2.0 / 1.0	2.0
Sulfate			5.0	5.0 / 2.5	5.0

Test	Range of Curve (mg/L)
Fluoride	0.20 - 2.0
Chloride	0.20 - 7.5
Nitrite-N	0.10 - 5.0
Bromide	0.10 - 5.0
Nitrate-N	0.10 - 4.0
O-PO4	0.20 - 4.0
Sulfate	0.20 - 10.0

IC Data Qualifiers used by the analyst in the raw data evaluation.

CE = **C**o-**E**lution or masking of peak(s) has been identified

OR = **O**ver **R**ange - Peak exceeds the highest standard of the calibration curve

OD = **O**ver **D**ilution - The ion is reported from a less dilute injection

NR = **N**ot **R**equired - analysis was not required for this ion

AD = **A**nalyst **D**iscretion was used in the evaluation and the reporting of the ion

RE = **R**eported **E**lsewhere

Analyst Signature: _____ Date: _____

Reviewer Signature: _____ Date: _____

Line	Sample	Sample Type	Level	Method	Data File	Volume
1	ICVI06AINIC9	Sample		dx-120.met	d5169_a001.dxd	1
2	ICB	Sample		dx-120.met	d5169_002.dxd	1
3	MB	Sample		dx-120.met	d5169_003.dxd	1
4	LCS	Sample		dx-120.met	d5169_004.dxd	1
5	243055-7	Sample		dx-120.met	d5169_005.dxd	1
6	243055-7MS	Sample		dx-120.met	d5169_006.dxd	1
7	243055-7MSD	Sample		dx-120.met	d5169_007.dxd	1
8	243221-5	Sample		dx-120.met	d5169_008.dxd	1
9	243301-4	Sample		dx-120.met	d5169_009.dxd	1
10	CCVI06AINIC10	Sample		dx-120.met	d5169_010.dxd	1
11	CCB	Sample		dx-120.met	d5169_011.dxd	1

020-002

Schedule File: C:\PEAKNET\Schedule\JAN1006.sch

Line	Dilution	Weight	Int. Std.	Comment
1	1	1	1	
2	1	1	1	
3	1	1	1	
4	1	1	1	
5	50	1	1	
6	50	1	1	
7	50	1	1	
8	20	1	1	
9	20	1	1	
10	1	1	1	
11	1	1	1	

Default Method Path: C:\PEAKNET\METHOD
Default Data Path: C:\PEAKNET\DATA\JAN1006
Comment:

020-003

1/10/06 13:44

Ion Chromatography Analysis
Method Code..: 300.0
Batch Code...: 170058

Status.....: RPT
Batch Date...: 01/10/06
Batch Time...: 1323

User Name.....: nrp
QC Code.....: 300
Calc Code.....: IC

Location Code..: 57222
Equipment Code.: IC4
Import Code....:

			TEST CODE	BRO	CHL	FL	NO3	SO4	NO2	OPO4	CLHIGH	S4HIGH										
SAMPLE: Grp Pos	Sample ID	Dilution	TEST POS Date / Time	10	11	12	13	14	15	16	17	18										
1 1	___ICV_I06AINIC9_	1.00	1/10/06 1007		0																	
1 2	___ICB__	1.00	1/10/06 1021		0																	
1 3	___MB__	1.00	1/10/06 1035		0																	
1 4	___LCS_I06AINIC9_	1.00	1/10/06 1049		0																	
1 5	243055_7____	50.00	1/10/06 1103		0																	
1 6	243055_7__MS_I06AINIC9_5	50.00	1/10/06 1116		0																	
1 7	243055_7__MSD_I06AINIC9_5	50.00	1/10/06 1130		0																	
1 8	243221_5____	20.00	1/10/06 1144		0																	
1 9	243301_4____	20.00	1/10/06 1158		0																	
1 10	___CCV_I06AINIC10_	1.00	1/10/06 1212		0																	
1 11	___CCB__	1.00	1/10/06 1226		0																	

020-004

Ion Chromatography Analysis

Report Date: 1/10/06 13:44

Method Code..: 300.0	Batch Date...: 01/10/06	QC Code.....: 300	Equipment Code.: IC4
Batch Code...: 170058	Batch Time...: 1323	Calc Code.....: IC	Import Code....:
Status.....: RPT	User Name....: nrp	Location Code..: 57222	

Grp	Smp	Sample ID	Pos	Test	Result	Known	Original	Alternate	QC Res	F	QC Res	F
1	1	___ICV_I06AINIC9_	11	CHL	3.2782	3.00			109			
1	2	___ICB__	11	CHL	0.0000							
1	3	___MB__	11	CHL	0.0000							
1	4	___LCS_I06AINIC9_	11	CHL	3.2237	3.00			107			
1	6	243055_7__MS_I06AINIC9_5	11	CHL	7.9875	3.00	4.6129		112			
1	7	243055_7__MSD_I06AINIC9_5	11	CHL	7.8620	3.00	4.6129	7.9875	108		3.6	
1	10	___CCV_I06AINIC10_	11	CHL	1.0894	1.00			109			
1	11	___CCB__	11	CHL	0.1270							

020-005

Ion Chromatography Analysis

Report Date: 1/10/06 13:44

Method Code..: 300.0	Batch Date...: 01/10/06	QC Code.....: 300	Equipment Code.: IC4
Batch Code...: 170058	Batch Time...: 1323	Calc Code.....: IC	Import Code....:
Status.....: RPT	User Name....: nrp	Location Code..: 57222	

SAMPLE:	Grp	Pos	Sample ID	Dilution	CHL mg/L	FL mg/L	NO3 mg/L	SO4 mg/L	NO2 mg/L
	1	1	___ICV_I06AINIC9_	1.00	3.2782	0.0000	0.0000	0.0000	0.0000
	1	2	___ICB__	1.00	0.0000	0.0000	0.0000	0.0000	0.0000
	1	3	___MB__	1.00	0.0000	0.0000	0.0000	0.0000	0.0000
	1	4	___LCS_I06AINIC9_	1.00	3.2237	0.0000	0.0000	0.0000	0.0000
	1	5	243055_7____	50.00	4.6129	0.0000	0.1669	0.7911	0.0000
	1	6	243055_7__MS_I06AINIC9_5	50.00	7.9875	0.0000	0.1598	0.7637	0.0000
	1	7	243055_7__MSD_I06AINIC9_5	50.00	7.8620	0.0000	0.1588	0.7440	0.0000
	1	8	243221_5____	20.00	1.6164	0.0000	0.1321	0.3705	0.0000
	1	9	243301_4____	20.00	2.5374	0.0000	0.0000	0.8346	0.0000
	1	10	___CCV_I06AINIC10_	1.00	1.0894	0.0000	0.0000	0.0000	0.0000
	1	11	___CCB__	1.00	0.1270	0.0000	0.0000	0.0000	0.0000

020-006

Attachment 4.

Example: Data Review Checklist

STL Chicago
INORGANICS – STL LIMS DATA REVIEW CHECKLIST **Test** _____ **Analytical Batch#** _____

Prep Batch # _____
(File by analytical batch #)

Batch Entry Date: _____ Analysis Date: _____ No. of Jobs in Batch: _____

Analyst / Primary Reviewer: _____ 1st Level Review Date: _____

Secondary Reviewer: _____ 2nd Level Review Date: _____

	PRI REV	SEC REV	COMMENTS
1) Analyst correct			
2) Instrument Code present			
3) Was Data Imported _____ Manually entered _____ Balance Interface Used _____			
4) Samples & all QC in order as analyzed?			
5) Sample Date/Time analyzed correct			
6) Reagent Codes present and Amount Spiked correct?			
7) Dilution factors all present and correct?			
8) Are correct Sample ID's used? Are all samples designated with a Blue P?			
9) Are correct QC ID's used? Are all QC designated with a Blue P?			
10) Are all QC correctly related to the samples?			
11) Do all entries match raw data?			
12) Is all QC calculated and are correct flags applied?			
13) Is an NCM needed? ICV, MB, LCS, LCSD, DU, MS, MSD, RPD out; holding time missed			NCM # _____ Approved By: _____ Initials
Raw Data: 1) Is AD Batch # is clearly noted?			
2) Are manual calculations and final results clearly shown?			
3) Are all errors crossed out with single line & initialed and dated?			
4) All unused portions of the page(s) Z'd out?			
5) Is data signed & dated by analyst & reviewer?			

Attachment 5.

Example: Retention Time Window Summary Table

STL Chicago

Retention Time Window Summary Table

Instrument:	IC4: DX-120	Method: DX120.met
Prep Batch:	1700580	
Date:	1/10/2006	

Analyst:	Nessa Pierce

Parameter	ICV RT Minutes	RT Window +/- 5 %	
Fluoride			
Chloride	3.77	3.58	3.96
Nitrite			
Bromide			
Nitrate			
Orthophosphate			
Sulfate			

Analyst Signature: Nessa R. Pierce Date: 1/10/06

Attachment 6.

Example: Data Export to LIMS: Keystroke Sequence

STL Chicago

Ion Chromatography .CSV Export to LabNet:

1. From "PeakNet MainMenu" (Click the TAB under the specific Instrument "DXLAN or ACI)
2. [Batch]
3. [Processing]
4. [Input]
5. Click on [Select] *(upper left)*
6. Find the data file you want to download & double click on it.
7. Select Process Method "from data files"
8. [Processing]
9. [Export]
10. [Browse]
11. Click on arrow by data and go to the folder you want to export data to: Octopus (E:)\Inorganic
12. Double Click on IC4 and find the file you are downloading and type .csv as the extension name on that file, then click [OK]
13. For Report Type indicate "Full" then [OK]
14. [Processing]
15. [Start]
16. After "batch processing completed" message, [x]
17. "Save changes to untitled", [No]

Attachment 7:

DoD QSM Version 3: Appendix DOD-B QC Requirements Summary
Table B-1 and Table B-10
(024-001 to 024-004)

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-1 Summary of QC Check Definitions, Purpose, and Evaluation – Inorganics (WC)

QC Check	Definition	Purpose	Evaluation
CCV	This verification of the initial calibration that is required during the course of analysis at periodic intervals. Continuing calibration applies to both external standard and internal standard calibration techniques, as well as to linear and non-linear calibration models	To verify that instrument response is reliable, and has not changed significantly from the current ICAL	If the values for the analytes are outside the acceptance criteria, the initial calibration may not be stable. Results associated with out-of-control CCV results require reanalysis or flagging
Demonstrate Acceptable Analyst Capability	Analyst runs QC samples in series to establish his/her ability to produce data of acceptable accuracy and precision	To establish the analysts' ability to produce data of acceptable accuracy and precision	The average recovery and standard deviation of the replicate must be within designated acceptance criteria.
Distilled Standards (one high and one low) (Cyanide only)	Standards are run through the distillation procedure and then compared to the undistilled standards' reported values	To check the efficiency of the distillation process.	Results must agree to within ± 15 % of the undistilled value before analysis can proceed
Duplicate Sample	Two identical portions of material collected for chemical analysis, and identified by unique alphanumeric codes. The duplicate may be portioned from the same sample, or may be two identical samples taken from the same site. The two portions are taken and prepared and analyzed identically.	To provide information on the heterogeneity of the sample matrix or to determine the precision of the intralaboratory analytical process for a specific sample matrix	To provide information on the heterogeneity of the sample matrix. The greater the heterogeneity of the matrix, the greater the RPD between the sample and the duplicate
ICAL	Analysis of analytical standards at different concentrations that are used to determine and calibrate the quantitation range of the response of the analytical detector or method	To establish a calibration curve for the quantification of the analytes of interest	Statistical procedures are used to determine the relationship between the signal response and the known concentration of analytes of interest. The ICAL must be successful before any samples or other QC check samples can be analyzed.
LCS containing all analytes required to be reported	A QC standard of known composition prepared using reagent free water or an inert solid that is spiked with analytes of interest at the midpoint of the calibration curve or at the level of concern.	To evaluate method performance by assessing the ability of the lab/analyst to successfully recover the target analytes from a control (clean) matrix.	This is a required QC Check. The inability to achieve acceptable recoveries in the LCS indicate problems with the accuracy/bias of the measurement system.
MS	A sample prepared by adding a know amount of targeted analyte(s) to an aliquot of a specific environmental sample	To assess the performance of the method as applied to a particular matrix	The lack of acceptable recoveries in the matrix spike often points to problems with the sample matrix. One test of this is a comparison to the LCS recoveries. If the corresponding LCS recoveries are within acceptable limits, a matrix effect is likely. The lab should not correct for recovery; only report the results of the analyses and the associated MS results and indicate that the results from these analyses have increased uncertainty
MSD	A 2nd replicate MS prepared in the lab, spiked with an identical, known amount of targeted analyte(s), and analyzed to obtain a measure of the precision of the recovery for each analyte	To assess the performance of the method as applied to a particular matrix and provide information of the homogeneity of the matrix.	When compared to the MS, the MSD will provide information on the heterogeneity of the sample matrix.
Matrix Verification sample (CR+6 only)	A pH adjusted filtrate that has been spiked with CR+6 eo ensure that the sample matrix does not have a reducing condition or other interferents that could affect color development	To ensure that the sample matrix does not have a reducing condition or other inteferents that affect color development	To verify the absence of an interference, the spike recovery must be between 85% and 115%. If the result of the verification indicates a suppressive intereference, the sample should be diluted and reanalyzed. If the interference persists after the sample dilution, an alternate method should be used.
MDL Verification Check	A low-level spike taken through the prep and analytical steps at approximately 2x the MDL used to verify that the laboratory can detect analytes at the calculated MDL	To validate the MDL on an ongoing basis	If the MDL verification check fails, reprep/reanalyze at a higher level to set a higher MDL or the MDL study must be repeated.

Table B-1 cont.			
QC Check	**Definition**	**Purpose**	**Evaluation**
MB	A sample of a matrix similar to the batch of associated samples in which no target analytes or interferences are present at concentrations that impact the analytical results.	To assess background interferences or contamination in the analytical system that might lead to high bias or false positive data.	This QC is used to measure lab accuracy/bias. The MB could indicate whether contamination is occurring during sample prep and analysis. If analytes are detected > ½ RL, reanalyze or B-Flag results for all samples in prep batch. For common lab contaminants, no analytes detected > RL. See DoD Box D-5; & Sec. D.1.1.1
MDL Study	The process to determine the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.	To determine the lowest concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.	MDLs must be established prior to sample analysis. The RL or LOQ is at least 3x the MDL. Used in combination with the MDL verification check to validate the MDL on an ongoing basis.
RT window position establishment for each analyte (chromatographic methods only)	Determination of the placement of the RT window (start/stop time) of each analyte or group of analytes as it elutes through the chromatographic column so that analyte identification can be made during sample analysis. This is done during the initial calibration	To idendify analytes of interest	Incorrect window position may result in false negatives, require additional manual integrations, and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified.
RT window verification for each analyte (chromatographic methods only)	A standard is used to verify that the width and position of the RT windows are valid so that accurate analyte identification can be made during sample analysis	To minimize the occurance of both false positive and false negative results at each calibration verification.	The peaks from the standard used are compared to the RT window established during the ICAL to verify that the analytes of interest still fall within the window.
RT window width calculate for each analyte and surrogate (non-MS chromatographic methods only)	Determine the length of time between the sample injection and the appearance of a peak at the detector. The total length of time (window) is established for each analyte or groups of analytes and is set for complete elution of analyte peaks. It is based upon a series of analyses and statistical calculations that establish the measured band on the chromatogram that can be associated with a specific analyte or group of analytes.	To ensure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the standards and sample matrix to be analyzed. It is done to minimize the occurrence of both false positive and false negative results	Used to evaluate continued system performance. Tight RT windows may result in false negatives and/or cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide RT windows may result in false positive results that cannot be confirmed upon further analysis.
Second source calibration verification	A standard obtained or prepared from a source independent of the source of standards for the initial calibration. Its concentration should be at or near the middle of the calibration range. It is done after the initial calibration.	To verify the accuracy of the initial calibration	The concentration of the 2nd source calibration verification, determined from the analysis, is compared to the known value of the standard to determine the accuracy of the ICAL. This independent verification of the ICAL must be acceptable before sample analysis can begin.

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

STL Chicago

DoD QSM Version 3: Appendix DOD-B Quality Control Requirements Summary

Table B-10: Inorganic Analysis by Common Anions: Method 9056

QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
IDOC	Per Instrument/Analyst	DoD acceptance criteria if available; otherwise method specific criteria	Correct / Repeat for those analytes which failed criteria	NA
MDL	Annually or quarterly MDL Checks performed	40 CFR 136B; MDL verification checks must produce a signal at least 3x the instrument's noise level.	Run MDL check at higher level and set MDL higher or reconduct MDL study	NA
RT window width calculated for each analyte	After method set-up and after major maintenance	RT width ± 3 times standard deviation for each analyte over 24 hour period	NA	NA
ICAL (min. 3 stds and one calibration blank)	Daily initial calibration prior to sample analysis	$r \geq 0.995$ for linear regression	Correct problem then repeat initial calibration	NA
2nd Source calibration verification (ICV)	Once after each ICAL	Value of 2nd source within ± 10% of expected value.	Correct problem and verify 2nd source standard. Rerun, if that fails, correct problem and repeat initial calibration.	NA
RT window position establishment for each analyte	Once per ICAL	Position shall be at midpoint of ICAL	NA	NA
RT window verification for each analyte	Each calibration verification	Analyte within established window	Correct problem, then reanalyze all samples since the last RT check. If they fail, repeat ICAL and resset RT window	NA
Initial calibration verification (ICV)	Daily before sample analysis, when eluent is changed, and with every batch of samples	All analytes within ± 10% of expected value and RTs within appropriate windows	Correct problem and repeat ICV, if that fails repeat initial calibration.	NA
Continuing Calibration verification (CCV)	CCV – After every 10 field samples and at end of analysis sequence. (DoD Box 58: CCV standards shall be at or below the middle of the calibration range)	within ± 10% of expected value (Data associated with an unacceptable CCV may be fully usable under the following conditions: 5. CCV (high bias) and samples ND, then raw data may be reported with appropriate flag 6. 2. CCV (low bias) and samples exceed maximum regulatory limit/decision level (DoD Box 60: Project specific permission from appropriate DoD personnel is required to report data generated from a run with noncompliant CCV.)	Correct problem, rerun CCV. If that fails, repeat ICAL and reanalyze all samples since the last good CCV (DoD Box 59...if the lab chooses to demonstrate the success of routine corrective action through the use of 2 consecutive CCVs, then the concentrations of the two CCVs must be a two different levels within the original calibration curve with at least one falling below the middle of the calibration range.)	NA
MB	One per prep batch	No analytes detected > ½ RL	Correct problem, then see criteria in box D-5; if required, reprep/reanalyze MB and all associated samples	Apply B-flag to all results for the contaminated analyte(s) for all samples in the associated prep batch
LCS (containing all analytes to be reported)	One LCS per prep batch	DoD specified QC criteria, if available	Correct problem, reprep/reanalyze the LCS and all samples in the associated prep batch for failed analyte, if sufficient sample is available	Apply Q-flag to specific analyte(s) in all samples in the prep batch.
MS	One per prep batch per matrix	Use DoD specified QC criteria for LCS	Examine the project-specific DQOs. Contact the client as to additional measures to be taken	Apply J-flag to specific analyte(s) in the parent sample
MSD	One per prep batch per matrix	RPD ≤ 20% (between MS and MSD)	Examine the project-specific DQOs. Contact the client as to additional measures to be taken	Apply J-flag to specific analyte(s) in the parent sample
Sample Duplicate	One per every 20 samples	% D ≤ 10% (between sample and sample duplicate)	Correct problem and reanalyze sample and duplicate	Apply Q-flag to specific analyte(s) in the parent sample

Table B-10 cont.				
QC Check	**Minimum Frequency**	**Acceptance Criteria**	**Corrective Action**	**Flagging Criteria**
Results reported between LOD and LOQ			Apply J-flag to all results between LOD (MDL) and LOQ (RL)	
Manual Integration (IC only)	When manual integrations are performed	Raw data shall include a complete audit trail for those manipulations, raw data output showing the results of the MI (i.e., chromatograms of manually integrated peaks), and notation of rationale, date, and signature/initials of person performing manual operation.		Apply M-flag to MI data

Notes:
1. Project-specific requirements identified by the client supersede any requirements listed. The requirements are meant to be default, to be used when project-specific direction based on DQOs is not available.
2. If there is a contradiction between the method and the DoD tables, the requirements specified in the tables shall be followed.
3. If the requirements in the DoD tables do not yet correspond with the most recent version of the SW-846 method, or a new method that analyzes for the same group of analytes becomes available, the requirements in the method shall be followed where appropriate.

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the laboratory procedure for the determination of total phosphorus (P) in non-potable water and solid and chemical materials. This procedure is based on the reactions that are specific for the orthophosphate ion. This SOP describes the persulfate digestion procedure, which results in the measurement of total phosphorus.

1.2 The reporting limit is 0.010 mg/L for waters and 2.00 mg/Kg for solids.

2.0 SUMMARY OF METHOD

2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid (persulfate digestion) that is proportional to the phosphorus concentration.

2.2 This procedure is based on EPA Method 365.2, Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Single Reagent, Issued 1971.

Modifications made to the procedure by the laboratory are listed below:

- Water samples with particulates are filtered after the addition of reagents and color development has taken place.
- Potassium persulfate is used in place of ammonium persulfate.
- A 100 mL sample volume is used with the addition of 2 mL of 30% H_2SO_4, and 1 scoop of potassium persulfate. The sample is split into two 50 mL portions, one of which is subject to color development. If dilutions are required, then the other 50 mL portion is used.
- Neutralization of samples and standards is performed with the addition of saturated base, phenolphthalein (3 drops), and 1N H_2SO_4. The pH is checked with pH paper instead of a pH meter.
- 10% HCL is used to clean glassware instead of hot 50% HCL.
- The test method recommends the analysis of calibration standards at the following concentrations in mg/L: 0.00, 0.01, 0.03, 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50. The concentration of the calibration standards used by the laboratory is: 0.00, 0.01, 0.02, 0.05, 0.10, 0.30, 0.50 and 0.70 mg/L.
- 1.06 g of ascorbic acid (crystal) is used in the combined reagent rather than 2 portions of 30 mL 0.1M Ascorbic acid.

3.0 DEFINITIONS

3.1 Definitions are included in Appendix A.

4.0 INTERFERENCES

4.1 Interferences may be caused by contaminants in the reagent water, reagents, and glassware. To minimize interferences, high purity reagents must be used and all glassware prepared following the procedures described in this SOP.

4.2 Sample turbidity must be removed by filtration prior to analysis for orthophosphate. Samples for total phosphorus may be filtered only after digestion. Sample color that absorbs in the photometric range used for analysis will also interfere.

5.0 SAFETY

5.1 Employees must be trained on and they must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2 Specific Safety Concerns or Requirements

None

5.3 Primary Materials Used

Table 1 provided in Section 18.0 lists those materials used in this procedure that have a serious or significant hazard rating along with the exposure limits and primary hazards associated with that material as identified in the MSDS. The table does not include all materials used in the procedure**.** A complete list of materials used can be found in Section 7.0. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS. Any questions regarding the safe handling of these materials should be directed to the laboratory's Environmental Health and Safety Coordinator.

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance, Top Loading; capable of accurately weighing to the nearest 0.01 g.

6.2 Balance, Analytical: capable of accurately weighing to the nearest 0.0001 g.

6.3 Hot plate.

6.4 Spectrophotometer suitable for measurements at 650 nm.

6.5 Cuvette: 2cm path length.

6.6 Erlenmeyer Flasks, 250 mL: used only for this test. Wash after use with 10% HCl solution, rinse with distilled water, and fill with a 10% HCl solution (2 L HCl to 18 L Reagent water). Segregate the glassware and use it only for this procedure. Never use commercial detergents.

6.7 Volumetric Flasks, Class A: 50, 100, 500 and 1000 mL

6.8 Pipettes, Class A: 1.0, 2.0, 5.0, 10.0, 50.0 mL

6.9 pH paper: pH range 1-14

7.0 REAGENTS AND STANDARDS

Unless otherwise specified assign an expiration date of six months from date of preparation to prepared reagent or standard unless the expiration date of the parent component expires sooner, in which case the earliest expiration date must be assigned. Store all standards at room temperature unless otherwise noted.

7.1 Reagents

Reagent Water

Potassium di-Hydrogen Phosphate (KH_2PO_4): Reagent Grade, J. T. Baker or equivalent

Phenolphthalein: Reagent Grade, Fisher brand or equivalent

Ammonium Molybdate ($[NH_4]_6Mo_7O_{24}.4H_2O$): Reagent Grade, J. T. Baker or equivalent

Antimony Potassium Tartrate ($K(SbO)C_4H_4O$ ½ H_2O): Reagent Grade, J. T. Baker or equivalent

Potassium Persulfate ($K_2S_2O_8$): Reagent Grade, J. T. Baker or equivalent

Isopropyl Alcohol: Reagent Grade, J. T. Baker or equivalent

Ascorbic Acid Crystals or Powder ($C_6H_8O_6$): Reagent Grade, J. T. Baker or equivalent

Sulfuric Acid (H_2SO_4): Concentrated, Reagent Grade, J. T. Baker or equivalent

Hydrochloric Acid (HCl): Concentrated, Reagent Grade, J. T. Baker or equivalent

Sodium Hydroxide Pellets (NaOH): Concentrated, Reagent Grade, J. T. Baker or equivalent

10% HCl: Add 2L of concentrated HCl to a carboy containing 18L of reagent water

30% Sulfuric acid: Slowly and carefully add 600 mL concentrated sulfuric acid, H_2SO_4, to approximately 1200 mL reagent water. Bring to 2 liters with reagent water. Cool before using.

Sulfuric Acid, 5N: Slowly and carefully add 257g (140 mL) of concentrated H_2SO_4 to approximately 700 mL of reagent water. Adjust volume to 1000 mL with reagent water.

Sulfuric Acid, 1N: Slowly and carefully add 28 mL of concentrated H_2SO_4 to approximately 900 mL of reagent water. Adjust volume to 1000 mL with reagent water.

Phenolphthalein Indicator: Measure approximately 1.0 g of phenolphthalein and mix with 100 mL of isopropyl alcohol. Allow phenolphthalein to dissolve before using.

Saturated Base: Weigh 1000 g NaOH pellets and slowly add to 1000 mL of reagent water. Allow pellets to dissolve, and cool before using.

Ammonium Molybdate Reagent: To a 500mL volumetric flask containing approximately 200mL of reagent water, add 20.0 g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$). Bring to volume with reagent water and mix well. Transfer to a plastic bottle and stored in the refrigerator.

Antimony Potassium Tartrate Reagent: Measure 1.3715 g antimony potassium tartrate ($K(SbO)C_4H_4O$ ½ H_2O) into a 500 mL volumetric flask. Bring to volume with reagent water. Transfer to amber glass bottle and store in refrigerator.

Combined Color Reagent: Measure and combine the following reagents in the listed order: 60 mL reagent water, 100 mL of 5N H_2SO_4, 10 mL Antimony Potassium Tartrate Reagent, 30 mL Ammonium Molybdate Reagent, and 1.06 g of Ascorbic Acid. Mix together until all Ascorbic Acid is dissolved. Combined Color Reagent is good for 2-3 hours, and will treat 24 samples.

7.2 Standards

Phosphorus Stock Standard (50 mg): Measure 0.2195 g of KH_2PO_4 into a 1000 mL volumetric flask. Adjust to volume with reagent water.

Phosphorus Intermediate Standard (1.0 mg): Dilute the 50 mg/L Phosphorus Stock Standard by adding 5.0 mL of the 50 mg/L standard into 250 mL of reagent

water. This standard is used to prepare the calibration curve, CCV, and the MS spike solution.

ICV/LCS Solution: The ICV/LCS solution is commercially obtained from a source separate from the standards used to make the calibration curve. The ICV/LCS is prepared at a difference concentration level than the CCV. A recommended standard is obtained from ERA and has a concentration of 0.40 mg/L

8.0 SAMPLE HANDLING AND PRESERVATION

8.1 A minimum volume of 100 mL sample should be collected in 500 mL plastic or glass containers and preserved to a pH < 2 with sulfuric acid. For soils, collect a minimum of 10 g in plastic or glass containers. Immediately following collection all samples should be cooled to 4˚C (±2) and maintained at that temperature until sample preparation and analysis.

8.2 The holding time for samples is 28 days from date of collection.

8.3 Unless otherwise specified by client or regulatory program, after analysis, samples are retained for 30 days and then disposed of in accordance with applicable regulations.

9.0 QUALITY CONTROL

9.1 A method blank (MB), laboratory control sample (LCS), matrix spike (MS), and sample duplicate (DP) are analyzed with each batch of 20 or less samples. For this test, the ICV serves as the LCS. The acceptance criteria for QC samples is provided in Table 2, Section 18.0 along with recommended corrective action.

9.2 Samples whose analytical results exceed the calibration range are diluted and reanalyzed.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Standard Curve

A calibration curve is prepared with each batch of samples processed.

Prepare the calibration standards by adding a known volume of phosphorus standard to a known volume of reagent water using the volumes specified in the following table:

Level	Phosphorus Standard (1 mg/L) (mL)	Reagent water (mL)	Concentration (mg/L)
Blank	NA	100	0.000
1	1.00	99.0	0.010
2	2.00	98.0	0.020
3	5.00	95.0	0.050
4	10.0	90.0	0.100
5	30.0	70.0	0.300
6	50.0	50.0	0.500
7	70.0	30.0	0.700

Digest and colorize the calibration standards following the procedures described in Section 11.0. Read the transmittance of each calibration level using the spectrophotometer. Prepare a calibration curve by plotting the transmittance against final concentration. Using linear regression, calculate a correlation coefficient (r). The correlation coefficient must be ≥ 0.995 for the calibration to be considered acceptable. If this criterion is not met, the calibration procedure must be repeated and re-digested along with all associated samples.

11.0 PROCEDURE

11.1 Equipment Preparation

Assemble and prepare the glassware that is designated for phosphorus analyses only. Rinse the glassware with 10% HCl solution, followed by reagent water.

11.2 Sample Preparation

Note: If digesting water and soil samples together, add the same amount of 30% sulfuric acid and potassium persulfate to the standards as added to the soil samples.

11.2.1 Water Preparation

Transfer each calibration standard to a labeled Erlenmeyer flask.

Transfer 100 mL of each sample into labeled Erlenmeyer flasks. Use 100 mL of reagent water for the method blank. Add 1.0 mL of the 50 mg/L phosphorus stock solution to each matrix spike, to result in a MS spike concentration of 0.5 mg/L P. Transfer an additional aliquot of the sample for which a duplicate analysis will be performed to a separate flask.

To prepare the ICV/LCS, transfer 100 mL of the ICV/LCS stock standard (0.40 mg/L) to a flask. An alternate concentration and source may be used for the ICV/LCS provided that the source is different than the source used for the calibration standards.

Add 2 mL of 30% sulfuric acid solution and 0.3 g (1 scoop) of potassium persulfate to each flask and swirl to mix.

11.2.2 Soil Preparation

Transfer each calibration standard to a labeled Erlenmeyer flask.

Measure 0.5 g of each sample into a labeled Erlenmeyer flask. Add 100 mL of reagent water to the flask and swirl to mix. Add 1.0 mL of the 50 mg/L phosphorus stock standard solution to the MS, to result in a MS spike concentration of 0.5 mg/L / 100 mg/kg P. Transfer an additional aliquot of the sample for which a duplicate analysis will be performed to a separate flask.

To prepare the ICV/LCS, transfer 90 mL of reagent water into a labeled Erlenmeyer flask and add 10.0 mL of the ICV/LCS stock standard (1.26 mg/L) to the flask. An alternate concentration and source may be used for the ICV/LCS provided that the source is different than the source used for the calibration standards. Use 100 mL of reagent water for the method blank.

Add 6 mL 30% sulfuric acid solution and 0.9 g potassium persulfate to each flask and swirl to mix.

11.3 Digestion

Place flasks on hot plates in the fume hood and adjust the temperature of the hot plate to maximum heat. Bring the samples to a boil and evaporate until the volume is ~50 mL or less. Ensure that flasks do not touch each other or splatter while on the hot plate. If excessive “bumping” occurs, reduce the heat. Monitor the digestion to ensure samples do not evaporate to dryness.

After the sample volume has been reduced to ~50 mL, remove the flask from heat and rinse the inner surface of the flask with reagent water. Allow the digestate to cool.

11.4 Colorization

Check the pH of each sample. Neutralize the sample with sodium hydroxide to pH 7 using 2-3 drops of phenolphthalein solution as an indicator. After the addition of phenolphthalein add single drops of saturated sodium hydroxide solution to each sample until a permanent pink color develops. After which, add single drops of 1N sulfuric acid solution until the pink color disappears. Add a single final drop of 1N sulfuric acid solution and swirl to mix. *Note: The color of soils samples may slowly return to pink again. If this occurs, add single drops of 1N sulfuric acid solution until the pink color disappears, then add a single final drop and swirl to mix.*

Transfer the digested sample from the Erlenmeyer flask to a 100 mL graduated cylinder and adjust the volume to 100 mL with reagent water. Transfer the sample back to the corresponding flask and swirl to mix.

Pour 50 mL of the sample digestate into the graduated cylinder and transfer the remaining 50 mL to a labeled tri-corner beaker. Repeat for each sample. After this step, there should be an Erlenmeyer flask and a tri-corner beaker for each sample digestate containing 50 mL each. ***Note****: For soil samples that may require dilution, pour 90 mL of digestate into the tri-corner beaker leaving only 10 mL in the Erlenmeyer. Then add 40mL Reagent water to the Erlenmeyer flask to yield a five-fold dilution that can be used if dilution is determined to be necessary.*

Add 8 mL combined color reagent to each Erlenmeyer and swirl to mix. Allow the color to develop for 10 minutes.

11.5 Analysis

Centrifuge and decant sample digestates that exhibit turbidity or contain suspended particulate matter. If it is necessary to filter a sample to remove material that will interfere with analysis, do so before colorization. Document these steps on the benchsheet.

Using the spectrophotometer, read the percent transmittance at 650 nm using a 2 cm cuvette. Start by zeroing the instrument, then read DI Water, the calibration curve, the ICV/LCS, the Method Blank, and the samples. Re-read the 0.100 mg/L calibration curve standard as a CCV and reagent water as CCB following every 10 samples and at the end of the run.

Record the readings on the bench sheet designated for this purpose. Samples must be read at least 10 minutes after color development and before 30 minutes have passed.

Samples with concentrations that exceed the linear range must be diluted and the colorization step repeated on the diluted aliquot. Sample digestates may be diluted up to one hundred fold. If the sample digestate requires a greater dilution, it is possible that the acid and persulfate were exhausted before complete digestion occurred and the digestion should be repeated using a smaller sample volume.

After analysis is complete, rinse the glassware with Reagent water and fill the Erlenmeyer flasks with 200 mL Reagent water. Add a sufficient volume of 10% HCl solution to fill the flask and cover with clean tri-corner beakers. Place the glassware in the designated storage area.

Calculate the concentration of target analyte in each sample by entering the transmittance readings, dilution factor, sample volume/mass and percent solids for each sample ID into the document controlled EXCEL spreadsheet created for

phosphorus calculations. Sample concentration is then determined from the entered values using linear regression analysis.

Quantitative results should be reported in appropriate units and significant figures and must be corrected for dilutions and percent solids.

12.0 CALCULATIONS

12.1 Aqueous Sample Concentration

$$\text{mg/L P} = \frac{\text{mg/L P}_{\text{digestate}} \times \text{Digestate Volume (mL)}}{\text{Sample Volume (mL)}}$$

12.2 Solid Sample Concentration

$$\text{mg/kg P (As Received)} = \frac{\text{mg/L P}_{\text{digestate}} \times \text{Digestate Volume (mL)}}{\text{Sample Volume (g)}}$$

$$\text{mg/kg P (Dry Weight)} = \frac{\text{mg/L P}_{\text{digestate}} \times \text{Digestate Volume (mL)}}{\text{Sample Volume (g)} \times \text{Percent Solids}}$$

12.3 Percent Recovery (%R)

$$\%R = \frac{SR}{SA} \times 100\%$$

Where:
SR= Sample Result
SA=Concentration of Spike Added

12.4 MS Percent Recovery

$$\text{MS Recovery(\%)} = \frac{SSR - SR}{SA} \times 100\%$$

Where:
SSR=Matrix Spike Result
SR=Sample Result
SA=Concentration of Spike Added

12.5 Relative Percent Difference (RPD)

$$RPD = \frac{|D_1 - D_2|}{\frac{D_1 + D_2}{2}} \times 100$$

Where:
D1 = Sample result
D2 = Matrix duplicate result

13.0 DATA ASSESSMENT, CRITERIA & CORRECTIVE ACTION

13.1 Review the samples, standards and QC samples against the acceptance criteria specified in Table 2, Section 18.0. If the results are not within criteria, corrective perform the recommended corrective action. If corrective action is not taken or unsuccessful, the situation should be documented and reported in the project narrative. All data that does not meet established criteria must be flagged with the appropriate data qualifier and noted in the project narrative.

14.0 METHOD PERFORMANCE

14.1 An Initial Demonstration of Capability is required for each analyst before unsupervised performance of this method.

14.2 A Method Detection Limit (MDL) determination for each test method referenced in this SOP is performed following the procedure described in the reference method, 40CFR, Part 136, Appendix B and laboratory SOP LP-QA-005. The MDL is verified or repeated when a significant change to the method occurs. Significant changes include the use of alternate reagents or standard reference materials, new instrumentation or the use of alternate sample preparation procedures.

15.0 POLLUTION PREVENTION & WASTE MANAGEMENT

15.1 Where reasonably possible technology changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this SOP and the policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 The following waste streams are produced when this method is carried out.

- Acidic Waste – 2.5L glass satellite container
- Contaminated disposable plastic ware – general trash stream

Transfer the waste stream to the appropriate satellite container(s) located in your work area. Notify authorized personnel when it is time to transfer the contents of the satellite containers to the hazardous waster storage room for future disposal in accordance with Federal, State and Local regulations, The procedures for waste management are further given in the laboratory SOP LP-LB-0010 *Hazardous Waste.*

16.0 REVISION HISTORY

16.1 Cover Page: Changed to reflect current management team.

16.2 Section 7.1: Added HCl (concentrated and 10%).

16.3 Section 12.0: Added calculations for sample concentration.

16.4 Section 16.0: Changed to Revision History

16.5 Section 17.0: Changed to References

16.6 Section 18.0: This section was added.

16.7 Throughout document: changed absorbance to transmittance

17.0 REFERENCES

17.1 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, 40 CFR Part 136, USEPA Office of Water.

17.2 EPA Method 365.2,Phosphorous, All Forms (Colorimetric, Ascorbic Acid, Single Reagent, Issued 1971.

18.0 TABLES, DIAGRAMS, FLOWCHARTS

18.1 Table 1: Primary Materials Used, Exposure Limits and Hazards
18.2 Table 2: QC Summary and Recommended Corrective Action
18.3 Appendix A: Terms and Definitions

Table 1: Primary Materials Used, Exposure Limits and Hazards

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

Table 2: QC Summary and Recommended Corrective Action

QC Sample	Frequency	Acceptance Limits	Corrective Action
ICAL	Beginning of analytical sequence	r $\geq$ 0.995	Standards check, re-calibration.
ICV/LCS	After ICAL	%R (85-115)	Check formulation of standards and ICV, re-prepare standards and/or ICV and re-analyze associated samples if required.
CCV	Every 10 samples and at the end of the analytical run.	%R (85-115)	Re-analyze once, if still outside limits bracketed samples are rerun with new ICAL.
CCB	Every 10 samples and at the end of the analytical run.	< Reporting Limit < ½ RL (DoD)	Re-analyze, if still above re-prepare and reanalyze batch.
Method Blank	Each batch of 20 samples or less.	< Reporting Limit < ½ RL (DoD)	Re-analyze, if still above re-prepare and reanalyze batch.
Matrix Spike (MS)	Every 20 sample batch	%R (85-115)	The MS is used to assess the effect of the sample matrix on the accuracy of the method. Evaluate any MS outside limits and note as a non-conformance if a matrix effect is indicated.
Matrix Duplicate (DP)	Every 20 sample batch	RPD $\leq$ 20	The DP is used to assess the effect of the sample matrix on the precision of the method. Evaluate any DP outside limits and note as a non-conformance if a matrix effect is indicated.

Appendix A: Terms & Definitions

Batch: environmental samples, which are prepared and/or analyzed together with the same process, using the same lot(s) of reagents. A preparation/digestion batch is composed of one to 20 environmental samples of similar matrix, meeting the above criteria.

Calibration Curve: the graphical relationship between the known values or a series of calibration standards and their instrument response.

Continuing Calibration Verification (CCV): a single or multi-parameter calibration standard used to verify the stability of the method over time.

Demonstration of Capability (DOC): procedure to establish the ability to generate acceptable accuracy and precision.

Holding Time: the maximum time that a sample may be held before preparation and/or analysis as promulgated by regulation or as specified in a test method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations used to define the quantitative response, linearity and dynamic range of the instrument to target analytes.

Initial Calibration Verification (ICV): solution prepared from a separate source from that which is used to prepare the calibration curve.

Intermediate Standard: a solution made from one or more stock standards at a concentration between the stock and working standard. Intermediate standards may be certified stock standard solutions purchased from a vendor and are also known as secondary standards.

Laboratory Control Sample (LCS): a blank matrix spiked with a known amount of analyte(s) processed simultaneously with and under the same conditions as samples through all steps of the procedure.

Matrix Duplicate (DP): duplicate aliquot of a sample processed and analyzed independently; under the same laboratory conditions; also referred to as Sample Duplicate.

Matrix Spike (MS): a field sample to which a known amount of target analyte(s) is added.

Method Blank (MB): a blank matrix processed simultaneously with and under the same conditions as samples through all steps of the procedure. Also known as the preparation blank (PB).

Method Detection Limit (MDL): the minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which relative uncertainty is ±100%. The MDL represents a range where qualitative detection occurs. Quantitative results are not produced in this range.

Non-conformance: an indication, judgment, or state of not having met the requirements of the relevant specification, contract or regulation.

Preservation: refrigeration and/or reagents added at the time of sample collection to maintain the chemical, physical, and/or biological integrity of the sample.

Reporting Limit (RL): the level to which data is reported for a specific test method and/or sample. The RL must be minimally at or above the MDL.

Stock Standard: a solution made with one or more neat standards usually with a high concentration. Also known as a primary standard. Stock standards may be certified solutions purchased from a vendor.

Total Phosphorus (P): all of the phosphorus present in the sample as measured by the persulfate digestion procedure.