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Final On-Site Laboratory Evaluation Report (SDWA)

Inorganic Chemistry

(Rev. 2-22-00)

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory Section
4710 Chimney Drive, Suite G
Charleston, WV 25302

November 30- December 1, 1999

Surveyed by:

Joseph Slayton
Robin Costas

U.S.E.P.A. - Region III
Office of Analytical Services and Quality Assurance
701 Mapes Road
Ft. Meade, Maryland 20755-5350

A. Introduction:

On November 30, 1999 an on-site inspection of inorganic chemistry was conducted of the West Virginia Department of Health and Human Resources, Bureau for Public Health, Office of Laboratory Services. The analyses of drinking water samples is conducted at a separate location, Environmental Chemistry Laboratory Section, 4710 Chimney Drive, Suite G, Charleston, WV 25302. The purpose of this inspection was to determine the capability of the laboratory to perform its mission as it relates to the Safe Drinking Water Act (SDWA). The laboratory was represented by Dr. Andrea Labik, Sc.D, Office of Laboratory Services Director, Dr. Wayne Morganroth, Laboratory Supervisor, Mr. Larry Duffield, Chemist II (analysis of metals), and Mr. Greg Young, Chemist I (analysis of inorganic, non-metal analytes).

This inspection was conducted by: Robin Costas, Chemist (evaluation of metals) and Joseph Slayton, Associate Director of Science (evaluation of inorganic, non-metals); USEPA, Region III, Office of Analytical Services and Quality Assurance, 701 Mapes Road, Ft. Meade, Maryland 20755-5350. In addition the Office of Municipal Assistance, Water Protection Division was represented by Mr. Jason Gambetese of the Philadelphia Regional Office (EPA).

Since the last on-site laboratory inspection performed by EPA in 1996, the Bureau of Public Health Laboratory has lost the capability to perform the analyses of organic contaminants for SDWA. In addition, the listing in Section E of this report, "Contaminant Method Information" is the subset of regulated and "unregulated" parameters for which the laboratory is requesting SDWA certification. As indicated in Section E, this requested list represents an abbreviated subset of the SDWA contaminants. Also, the Director of the Office of Laboratory Services, Dr. Frank Lambert, Jr. and the Associate Director of the Division of Environmental & Newborn Laboratory Services have both retired. The new Director, Dr. Andrea Labik, was appointed in October 1999. The Associate Division Director position has not yet been filled.

Compliance samples for total nitrate are routinely analyzed and reported as a sum for (NO2+NO3)-N. The State uses a concentration of 0.5 mg/L to "trigger" the immediate resampling and reanalysis, i.e., this may indicate an NO2-N concentration of 0.5 mg/L which has a maximum concentration limit of 0.5 mg/L. This approach will be discussed with the Region III Drinking Water Program Office to assure compliance with SDWA regulations.

B. Personnel:

The courtesy and professionalism of the laboratory personnel was greatly appreciated by the inspection team. It was apparent from the excellent record keeping and quality control procedures, that the laboratory personnel are dedicated to achieving analytical excellence.

C. Proficiency Testing (PT) Samples:

The laboratory data for Proficiency Testing samples for the years 1997 thru 1999 were discussed

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during the on-site evaluation. The laboratory results were "Acceptable" for all regulated inorganic parameters reported with the exception of the following "Not Acceptable" results: September 1997-sulfate; March 1998-nitrite, -O-PO4, -sulfate; September 1998- O-PO4 (nitrate and sulfate - acceptable); 1999- fluoride (O-PO4 not analyzed).

The laboratory indicated problems with the equipment used for fluoride (electrode) and imprecision in using the turbidimetric technique for sulfate. The laboratory has stopped using these techniques and is requesting certification for EPA Method 300.0, Ion Chromatography (IC). The laboratory does not perform ortho- phosphorus analyses and is not requesting certification for this analyte. The laboratory results in 1999 by IC was acceptable for sulfate but not acceptable for fluoride by IC. The problem with fluoride was associated with an interference at the beginning of the chromatographic run called the "water dip". The laboratory indicated that this problem had been corrected.

D. Analytical Method References:

The list of parameters in Section E were audited during this inspection with the associated methodology cited as follows:

(SM) - Standard Methods for the Examination of Water and Wastewater, 18th edition.
(EPA83) - Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79/83.
(EPA93) - Determination of Inorganic Substances in Environmental Samples, Aug 1993, EPA/600/R-93/100.
(EPA94) - Methods for the Determination of Metals in Environmental Samples, May 1994, EPA/600/R-94/111.
(CLADW) - Manual for the Certification of Laboratories Analyzing Drinking Water, March 1997, EPA 815-B-97-001.

E. Contaminant Method Information:

Primary Contaminants:

Parameter	Method	Instrumentation
Antimony	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Arsenic	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Barium	ICP (EPA94, 200.7)	Varian Liberty 100
Beryllium	GFAAS (SM 3113B)	Varian SpectraAA - 400 Plus
Cadmium	GFAAS (SM 3113B)	Varian SpectraAA - 400 Plus
Chromium	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Copper	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Lead	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Mercury	Cold Vapor AA (EPA94, 245.1)	PE-50B W/PE CVAAS
Selenium	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Sodium	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Thallium	GFAAS (EPA94, 200.9)	Perkin-Elmer 5100, HGA 600
Fluoride	EPA 300.0	Dionex-120; AS-40 Autosampler

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Nitrate	Automated Cadmium (EPA 353.2)	Technicon Auto-Reduction Analyzer II
Nitrite	Automated Cadmium (EPA 353.2)	Technicon Auto-Reduction Analyzer II
Turbidity	Nephelometric (EPA 180.1)	Hach Ratio Turbidimeter Model 2100A
Conductance	Conductance (SM 2510B)	Model 31 Conductivity Bridge

E. Contaminant Method Information (Cont.):

Unregulated Contaminants:

Parameter	Method	Instrumentation
Nickel	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus

Secondary Contaminants:

Aluminum	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Chloride	EPA 300.0	Dionex-120; AS-40 Autosampler
Iron	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Manganese	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Silver	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
TDS	EPA 160.1 Gravimetric	Gelman A/E GF Filters; Blue M Oven; Mettler AG-245
Zinc	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Sulfate	EPA 300.0	Dionex-120; AS-40 Autosampler

F. Calibration & Detection Information:

Maximum Contaminant Level (MCL), Method Detection Limit (MDL), Reporting Limit (RL as defined by the WV Laboratory, See Section I, Metals)

Primary Contaminants; Lead and Copper Rule; Sodium and Turbidity:

Contaminant	***Calibration Standards*** **(mg/L)**	**MCL(mg/L)**	**MDL(ug/L)**	**RL(ug/L)**
Antimony	BLK; 0.003; 0.006; 0.012	0.006	0.46	3
Arsenic	BLK; 0.002; 0.005; 0.010; 0.020	0.050	0.81	2
Barium	BLK; 0.50; 5.00; 10.0	2.00	0.000135	5
Beryllium	BLK; 0.0002; 0.0005; 0.001; 0.002	0.004	0.04	0.2
Cadmium	BLK; 0.001; 0.002; 0.004	0.005	0.07	1

Primary Contaminants; Lead and Copper Rule; Sodium and Turbidity (Cont.):

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Contaminant	*Calibration Standards* (mg/L)	MCL(mg/L)	MDL(ug/L)	RL(ug/L)
Chromium	BLK; 0.001; 0.0025; 0.005; 0.010	0.100	0.37	1
Copper	BLK; 0.001; 0.0025; 0.005; 0.010	1.3*	0.16	1
Lead	BLK; 0.001; 0.0025; 0.005; 0.010	0.015*	0.86	1
Mercury	BLK; 0.0002; 0.0005; 0.001; 0.002	0.002	0.065	0.2
Selenium	BLK; 0.002; 0.005; 0.010	0.050	0.30	2
Sodium	BLK; 2.0; 5.0;10.0;15.0; 20.0;30.0;50.0;100.0	20.0+	0.07	2000
Thallium	BLK; 0.002; 0.004; 0.008	0.002	0.65	1
Fluoride	BLK; 0.05; 0.1; 0.25; 0.50; 1.00	4.0	TBD	50
Nitrate	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	10.0	9.5	50
Nitrite	Cd Column Check Standard (1.0)	1.0	3.6	50
Turbidity	0.2; 0.4; 0.6; 0.8; 1.0 2; 4; 6; 8; 10 NTU	-	-	0.2NTU
Conductance	0.01N (1413 umhos/cm)	-	-	-
TDS	NIST Traceable Std. Wts.	[500]	-	-
Chloride	BLK; 5; 10; 15; 25; 30	[250]	TBD	500
Sulfate	BLK; 1; 4; 10; 20; 30	[250]	TBD	100

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* "Action Level"
+ "Reportable Level"
"TBD" = To Be Determined

G. Quality Control (QC) Procedures:

The laboratory follows a "Quality Assurance Program Plan for Chemistry Aspects of the West Virginia Bureau for Public Health", (QA Manual, Rev. 1/98). This document includes: instructions for sample submission to the laboratory (containers, preservations, sample handling procedures); instrument calibration; analytical procedures; data reduction; data validation and data reporting; data storage; preventive maintenance; internal QC checks and frequency; corrective action; precision and accuracy samples; and sample rejection policy. A partial list of the QC procedures observed during this inspection included: calibration records for thermometers; on-going temperature records of refrigerators and drying ovens; analysis of an external QC sample with each analytical batch; method detection limit determinations; duplicate analysis (precision measure); spike analysis (accuracy/recovery measure); blank analysis/batch; check standards at 10% frequency (instrument drift measure); instrument "run logs"; cadmium column reduction efficiency measured and recorded; standard weights employed to verify balance performance; detailed/clearly written and quickly retrieved analytical records; and resistance/conductivity of lab pure water recorded each day of use.

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H. Analytical Deviations:

Deviations are those laboratory techniques not in compliance with the mandatory requirements of the analytical methods cited above or with the 1997 EPA Manual for the Certification of Laboratories Analyzing Drinking Water, Fourth Edition, EPA/815-B-97-001, (referred to as CLADW). In addition, procedures/techniques, which are considered critical by the inspectors for the production of quality data are cited as "Good Laboratory Practices" (GLP). The following changes are required for the laboratory to maintain in compliance with the SDWA program (40 CFR 142.10):

General:

1. The principle WV state SDWA laboratory must maintain capability and certification for all the contaminants specified in the State Primary Drinking Water Regulations, p. E-1 CLADW, unless the State has been granted wavers for compliance monitoring of these analytes or has contracted with laboratories which are SDWA certified (by EPA or by a state other than WV) for these analytes. A listing of commercial laboratories employed by the State for SDWA compliance monitoring for the analytes not measured at the WV Lab and their current SDWA Certification status (State in which they hold certification, method and analytes) is necessary to complete our records.

2. Many of the QC acceptance/action limits for inorganic-non-metals where fixed limits. However, these criteria were not included in corresponding Standard Operating Procedures (SOPs), e.g., correlation coefficient limit of 0.995 for NO3. The QC limits must be included in the SOP. In addition, the corrective actions to be taken when limits are exceeded should be added to the SOP. The QA Plan only lists a general approach, the SOP needs to list specifics, e.g., stop analysis, take corrective action to correct problem with new reagents, new calibration standards, new pump tubes, new photo multiplier or colorimeter bulb, etc. Also, the SOP should specify that when QC limits are exceeded that all analysis since the last acceptable QC check are to be repeated.

3. Checks of sample preservations, required by CLADW must be recorded, GLP.

4. The laboratory has a Sample Rejection Policy. The laboratory must reject samples not preserved as per CLADW, e.g., turbidity, or the data must be flagged indicated that required preservation was not employed and/or required technical holding times were not met.

ICP Analyses:

5. All samples prepared for ICP analysis must be digested as according to method, ie. the addition of 2 mL (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid. This would translate into 700 uL of nitric acid and 350 uL of hydrochloric acid per 35 mL of sample. (EPA94, 200.7,

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Hardness?

11.2.3)

NO2-N & NO3-N:

6. The SOP must be updated to reflect the current EPA methods manual cited by 40 CFR, which is entitled: Determination of Inorganic Substances in Environmental Samples, Aug 1993, EPA/600/R-93/100.

7. Stock calibration solutions must be labeled with the date of preparation, analyst and expiration date. Stock solutions should not be retained more then a month (4C) unless verified to be accurate versus a newly prepared QC sample/ampule, GLP. Similarly, calibration standards are to be prepared fresh with each analytical batch of samples or the accuracy of the standards verified accurate versus a newly prepared QC sample /ampule, GLP.

8. The samples for nitrite-nitrate must be checked and verified free of chlorine or dechlorinating reagent must be added, EPA 353.2, EPA-600/R-93-100, August 1993.

Ion Chromatography (fluoride, chloride, sulfate):

9. Since the last Proficiency Testing sample for fluoride was "Not Acceptable" it is critically important that the laboratory purchase, analyze and forward PT results to EPA which demonstrate "Acceptable" performance, prior to the analysis of additional compliance samples.

10. MDLs have not been determined for the Ion Chromatography (IC) analytes. MDLs are required under SDWA regulations CLADW and EPA Method 300.0

11. An SOP must be prepared for IC analyses, GLP. This can be very brief, with sections referencing EPA Method 300.0 and listing any procedures differing from the referenced method. Where options are listed in the reference method, the SOP must indicate which option/s are actually employed by the laboratory.

12. Samples for sulfate are not refrigerated. Compliance samples are to be transported on ice as per CLADW.

13. An initial demonstration of capability is required for each analyte as per Section 7.2.7 CLADW and as detailed in 300.0.

14. The laboratory has purchased an IC (the first for the lab), but the analyst has not had previous experience with this technology. It is very important that the analyst have formal training available from the instrument manufacturer. It may prove cost effective to host a training course at the WV laboratory (Chimney Drive).

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Turbidity:

15. Samples arrive without refrigeration and are held longer then 48 hours. Compliance samples must be maintained at 4C from the time of sampling and analyzed within 48 hour, CLADW.

16. The SOP is dated and does not reference the current required method. The SOP must be updated to reference EPA-600/R-93-100, August 1993.

17. A reagent blank is not analyzed. A blank must be analyzed as per CLADW, however, values below the lowest calibration standard are to be reported as per the current practice (< lowest calibration standard).

Total Dissolved Solids (TDS):

18. Samples are received without refrigeration. Compliance samples for TDS analyses must be maintained at 4C from the time of sampling, CLADW.

Conductance:

19. Samples for conductance are received without refrigeration. Compliance samples for Conductance must be maintained at 4C from the time of sampling, CLADW.

I. Recommendations:

These items are offered as suggestions (not required):

General:

a. It is growing ever more critical that the laboratory managers and staff have access to the Internet. The EPA's web page is a vital source of information, e.g., current and projected SDWA regulations. Much information/communications within Region III are via E-Mail and such contacts are considered critically important to the State's Drinking Water Programs. In addition, since the analysts also serve as SDWA Lab Certification officers, the Internet would be an efficient and effective way to stay in communication with and distribute information to the drinking water laboratories in WV.

b. The QA Manual should be updated to reflect the current analytical procedures. Also, for this update it is recommended that the laboratory consider the sections required by the National Environmental Laboratory Accreditation Conference/Program (NELAC) for a Quality Manual. NELAC is an established program with consensus agreement of over 40 states and is consistent

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with international requirements (ISO025) for certification of environmental laboratories. The information for accreditation of WV's Laboratory under NELAC is available in Chapter 5, Quality Systems, of the NELAC standard and the details are available on the NELAC website at www.epa.gov\ttn\nelac. Other specific suggestions include: indication that records will be maintained for at least 5 years; addition of an additional "path" for the corrective action section for when corrective measures do not succeed (e.g., flagging associated data); eliminate corrective action flow chart for organic analytes and add one for inorganic analytes; addition of an organizational chart; reference/s to job description/s; description of training and training plans; list of SOPs; list of signatories for SOPs; requirements for chain-of-custody; list of references, especially for methods; list of tests for which an Initial Demonstration of Capability had been successfully performed.

c. The SOPs are being updated to reflect changes in referenced methods, e.g., NO2+NO3, and changes in technology/method, e.g., IC. It is suggested that the format of the SOP be expanded to include the topics required for method SOPs in the NELAC standards.

d. The ethyl ether stored in the laboratory freezer should be removed. The material may be explosive due to the spontaneous formation of peroxides.

e. The laboratory management should continue in their efforts to replace the vacant Associate Director position. The position is important to the effective coordination and prioritization of the efforts within the Environmental Chemistry and Microbiology Sections. In addition, this position has served to coordinate and oversee WV's SDWA Laboratory Certification Program.

f. An internal peer review should be performed on the inorganic analytical data and the laboratory should begin routine/systematic review/audits of analytical procedures for compliance with the QA manual and the SDWA regulations.

Metals:

g. No value which falls below the calculated MDL should be used in any quality control calculations, ie. do not use these numbers to calculate the Percent Recovery for the Analytical Spike. The concept is that values below the MDL are considered "non-detectable" and, therefore, are not reliable for quality control purposes.

Although, the data being produced is of excellent quality, the reason this is an issue is because of the low Reporting Levels (RL) the analyst is trying to achieve. Some of the MDL levels are very close to the RL and the concern is that the determined MDLs may be biased high for some contaminants. It is suggested that the MDLs be re-analyzed for those contaminants with high MDL levels and low RLs, such as lead, thallium, antimony, chromium. One alternative is to increase the RL (thallium and barium) and extend the linear range of the calibration curve where the Maximum Contamination Level (MCL) will allow.

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The following are some excerpts from some documentation which might help clarify issues about the MDL and RL determinations:

CLADW, 7.2.11: "Laboratories may prefer not to report contaminants at levels less than two to three times their MDL or below the level at which they routinely analyze their lowest standard."

CLADW, H-6, 2.3.3: "Although 40 CFR 136, Appendix B, provides several possible approaches to *selecting an estimated detection limit* (inspector's emphasis) for purposes of designing the MDL study...the most reliable method involves an iterative process of measuring achievability of successively lower concentrations until the actual limit of detection is identified. At a minimum, this approach should be used for purposes of establishing the working MDL when a new method is first used by a laboratory." and "The spike concentration should be determined by the signal to noise ratio for each analyte. The same concentration for all analytes will not produce acceptable results. The extractions/analyses should be performed over a period of at least three days to provide more reasonable MDL."

Guidance for Permit Writer's, Appendix B, 1.1: "The Minimum Level (ML) is a term that originated in the EPA 1600 Series methods, and is defined as the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure..."

Guidance for Permit Writer's, Appendix B, 3.1: "Once the permittee has developed a discharge-specific MDL for each analyte, this MDL is translated into a calculated interim ML by multiplying the discharge-specific MDL by a factor of 3.18. The calculated interim ML is rounded to produce the final interim ML." Although, this definition is from a guidance document for the NPDES program, it does give some explanation on the relationship between the MDL concentrations and what should be an expected quantification level for routine analysis. (National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantification Levels, March 22, 1994, EPA Draft document).

h. According to the CLADW (page H-4, section 2.3), the Initial demonstration of Capability (IDC) "consists of demonstrating proficiency in four areas: precision, accuracy (bias), method blank background, and method detection limit." It also suggests that labs "should maintain complete records for the IDC which include the bullet items in the Checklist." The Checklist, found on page H-15, section 2.3, describes an Initial Demonstration of Capability as "a minimum of four replicates of a quality control or reference samples processed through all steps of the analytical procedure."

It is highly recommended that the analyst perform this procedure for each contaminant using a known quality control sample. When four aliquots are digested and analyzed, both precision and accuracy measurements can be determined. All IDC records should be

Freedom_0006095_0011

maintained at the laboratory for future review.

i. The digestion logbook should be self-explanatory and include all relevant information about the particular set of samples and the digestion procedure used. The following are suggested additional column headings which would help clarify the work performed: Digestion Type, Block Temperature, Blanks Digested (y/n), LFB Digested (y/n).

NO2+NO3)-N:

j. The MDL study should be repeated with the spike at or slightly above the concentration of the quantitation range (concentration of the lowest calibration standard). The current MDLs were based on spikes at 0.003 mg/L which were below the lowest calibration standard (0.050 mg/L)

J. Certification Status:

Certified:

Arsenic; Antimony; Barium; Beryllium; Cadmium; Chromium; Copper; Lead; Mercury; Selenium; Sodium; Thallium; Nitrite; Nitrate.

Provisionally Certified:

Fluoride; Turbidity; Conductance.

Secondary Analytes:

Acceptable with Minor Deficiencies (Sulfate; Chloride; TDS).

K. Inspectors:

Joseph Slayton 2-22-00
Joseph Slayton Date

Robin L Costas 2.22.00
Robin Costas Date

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Final SDWA Lab Certification Program: On-Site Review

Rev. 2-21-00

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory Section
167 11th Avenue
South Charleston, WV 25303

December 1-2, 1999

Joseph Slayton
Associate Director Science

U.S.E.P.A. - Region III
Office of Analytical Services and Quality Assurance
701 Mapes Road
Ft. Meade, Maryland 20755-5350

Introduction:

On December 1-2, 1999 an on-site review of West Virginia's SDWA Laboratory Certification Program was conducted of the West Virginia Department of Health and Human Resources, Bureau of Public Health, Office of Laboratory Services. Laboratory SDWA certifications for inorganic and organic chemistry are conducted by Dr. Wayne Morganroth, Laboratory Supervisor, with the assistance of Mr. Larry Duffield, Chemist II and Mr. Greg Young, Chemist I. Laboratory SDWA certifications for microbiology are conducted by Mr. Thomas Ong, Microbiologist Supervisor, and Ms. Joyce Vance-Abshire, Microbiologist III.

This review was conducted through interviews, records/file review and Standard Operating Procedures (SOP) review. A joint inspection with the WV Laboratory Certification Program was planned for a local commercial laboratory but was not performed (See Section #3, in this report).

This review was conducted by Joseph Slayton, Associated Director of Science, USEPA, Region III, Office of Analytical Services and Quality Assurance, 701 Mapes Road, Ft. Meade, Maryland 20755-5350.

Personnel/Training/Vacancies:

Since the last oversight review performed by EPA in 1996, the Bureau for Public Health Laboratory has lost the capability to perform the analysis of organic contaminants for the SDWA. The inspection program lost the Certification Officer (CO), Ms. Brenda Barnett, who had hands-on experience with the SDWA organic protocols. Since the last inspection Dr. Wayne Morganroth, a SDWA CO for inorganic chemistry, has successfully completed the requirement as a Certification Officer for Organic Chemistry (Letter dated July 8, 1999 from Dr. M. Kate Smith, Ecological Exposure Research Division, National Exposure Research Laboratory, Cincinnati, Ohio). Similarly, the Microbiology section lost a CO in 1999, but Ms. Joyce Vance-Abshire has successfully completed the Certification Officer requirements for Microbiology (letter dated July 19, 1999 from Dr. M.K. Smith). Charlotte Billingsley, Associate Director, Division of Environmental & Newborn Laboratory Services, and the Director of the Office of Laboratory Services, Dr. Frank Lambert, both retired within the last few months. The Associated Director had the responsibility to oversee WV's SDWA laboratory certification program. Dr. Andrea Labik, was appointed as Director in October, but the Associate Director position has not yet been filled.

Overview:

The WV Laboratory Certification Program is based upon the Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures Quality Assurance, EPA 815-B-97-001, March 1997 and upon the 40 CFR Part 141-143 SDWA requirements, as well as, the analytical methods referenced in these documents. This includes the requirement that laboratories successfully analyze at least one proficiency testing sample per analyte (recently changed in the CFR to "per method") per year and have procedures and documentation, which

are found satisfactory by an on-site inspection by State COs at least once every three years. All of the SDWA Certification Officers are trained professionals with years of laboratory experience. In the case of chemistry, those inspectors not yet "certified" as COs by the EPA are accompanied by Dr. Morganroth who has the responsibility for review and sign-off on the recommendations from Mr. Larry Duffield and Mr. Greg Young. It is planned that Mr. Duffield attend the EPA CO's training course in 2000 and Mr. Young is to attend in 2001.

Certification Program Documentation:

The SOP/ QA Manual for WV's Microbiology Section includes a number of items relevant to the documentation of the Microbiology Certification Program. The topics in the SOP/QA Manual (Rev. 11/29/99) include: Mission Statement; Organizational Chart (Chain-of-Command); Position Requirements for Environmental Microbiology; Position Responsibilities; Personnel Performance (on-the-job-training; testing; performance evaluations); Technical Performance (demonstrated performance by labs to be certified); Laboratory Safety; Chart for Determining Certification Status; Laboratory Certification Officers (qualifications); Performance Evaluation form (used for the evaluation of analysts). The QA Manual for WV's Environmental Chemistry includes few topics relevant to the Chemistry Certification Program. The chemistry laboratory QA manual includes: instructions for sample submission to the laboratory (containers, preservations, sample handling procedures); instrument calibration; analytical procedures; data reduction; data validation and data reporting; data storage; preventive maintenance; internal QC checks and frequency; corrective action; precision and accuracy samples; and sample rejection policy.

In Addition, the WV laboratory certification program has developed an SOP/QA manual entitled: "Drinking Water Certification Program-Microbiology". This document included the following topics: Introduction (cites various supporting federal regulations and the use of the EPA Lab Certification Manual as the focus for the WV Microbiological program); Laboratory Certification Officer (qualifications); Certification Parameters; Certification Renewal (table listing forms, mailing label files, etc.); On-site Evaluations (checklists, procedures, reports, follow-up, etc.); Adding a Certified Laboratory (In-State); Adding a Certified Laboratory (Out-of-State); Performance Evaluation Samples (indicated as "UNDERGOING MAJOR REVISION"); Records Retention and Storage; Drinking Water Laboratory Certification Renewal (form); Laboratory Information Form: Drinking Water Laboratory Certification Renewal*FINAL NOTICE* (form); Drinking Water Certificate; Water Survey Schedule (template to track projected on-site inspections); Presurvey Package (cover letter and pre-survey form); On-site Inspection Report (template); On-site Evaluation Checklist; Follow-up Letter (reminder notice template for response to the on-site inspection); Follow-up Letter (2) (template for responses that were not acceptable); tracking chart for on-site evaluations (tracking corrective actions and correspondence associated with on-site inspections); Application for Laboratory Certification (form); Letter in Response to Out-of-State applications (Note: includes WV's approach to "Reciprocity"); Letter Noting Receipt of Application (form letter); Key to List of Approved Tests (the WV Laboratory CertificationProgram groups analytes for certification); Listing of Labs Certified in WV (listed by analyte groups for both Microbiology and Chemistry).

Observations & Suggestions:

1. Proficiency Testing (PT) Samples: The WV Laboratory Certification Program (WVLCP) has not decided on the details of operating the new PT program (the EPA no longer provides PE/PT samples). The WVLCP should establish a schedule for laboratories to participate in Water Supply studies. Since these samples are now available from commercial vendors, which provide them on a rapid schedule (some as frequently as every month), laboratories will have a great deal of flexibility in scheduling and securing these materials. In addition, the laboratories within the state would benefit from a letter/E-Mail explaining the details of WV's approach to the PT program. In addition, the WVLCP should include the specific plans for the PT program in a written SOP that includes: the scheduling; tracking; follow up and documentation trail and filing system for the PT program. The usefulness/efficiency of an electronic data base for storage of this information should be explored. In addition, since the State has the option under the new PT system to select a PT provider, probably the WV CLP could have the provider directly "populate" WV's PT data base with the individual laboratories results (disk and/or on-line).

2. On-site Laboratory Inspections: The WVLCP should maintain a record which lists the dates of inspections, analytes/analyte groups reviewed, certification status and the target/projected/estimated date (at least quarter) for the next on-site. Currently such information is maintained in an on-going table for Microbiology but a similar tabulation should be considered for Chemistry.

Ten laboratories will require on-site inspections for chemistry during 2000. Two of these laboratories are significantly beyond the required three year period. After the next round of chemistry inspections is completed, the WVLCP should consider working out a schedule of on-site inspections so that they do not all occur in the same year. Microbiology already has a staggered schedule.

3. Internet: The WVLCP has not had routine access to the Internet. It is growing ever more critical that the COs have access to the Internet. The EPA's web page is a vital source of information, e.g., current and projected SDWA regulations. Much information/communications within Region III are via E-Mail and such contacts are considered critically important to the Region III States' Drinking Water Programs. The Internet would be an efficient and effective way to stay in communication with and distribute information to the drinking water laboratories in WV. The laboratories should be encouraged to have access to the Internet- most will have some mode of access.

This review included a scheduled inspection of a laboratory, Bio-Chem Testing Inc., Putnam Village, Unit 23, Treys, WV 25569. Upon arrival at the laboratory, it was found that the laboratory infrequently performed SDWA analyses (only one set in over a year) and that the laboratory was unaware of new methods required by SDWA. The laboratory elected to postpone the inspection until they had come up to speed on the new methodologies; and therefore the

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items listed in the NELAC standards should further help assure a quality laboratory inspection program for West Virginia.

Inspector:

2-22-00

Joseph Slayton Date

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review of the WV Lab Certification-Chemistry did not include observation of an actual inspection. The WVLCP needs to assure that the laboratories in the program are informed of the current SDWA requirements. An internet/electronic mode of correspondence should be considered.

4. Documentation: The documentation for the Microbiology Certification Program was complete and well organized. The Chemistry Certification Program lacked written procedures for Lab Certification (as detailed above for Microbiology). It is suggested that an SOP/QA Manual for the drinking water laboratory certification chemistry program be prepared.

Given the reality that the current COs lack first hand experience with SDWA organic analyses, it is suggested that efforts to develop method specific checklists should be continued. These should be standardized and made available to all the COs involved (electronic format for ease of distribution and updating). Such checklists are also available from the USEPA and from other Region III State COs.

5. Personnel: Given that Dr. Morganroth alone can certify laboratories to perform organic analyses in West Virginia, it is critically important to the WV Laboratory Certification Program to assure that Mr. Larry Duffield and Mr. Greg Young are approved as Certification Officers for organic chemistry, as well as inorganic chemistry as soon as possible. In addition, since the Associated Director position serves as the central focal point for the WV Lab Certification Program, it is important that this vacancy be filled as soon as possible. The WV Laboratory Certification Program may benefit from the selection of an Associated Division Director with experience in SDWA related chemistry (especially organic chemistry).

The WVLCP should consider the benefits of providing administrative/clerical support to the chemistry and microbiology laboratory certification efforts, since the chemists and microbiologists are spending considerable time tracking and filing information. A part-time aide/clerk may benefit the program.

6. NELAC: As described previously, the WV's Laboratory Certification Program for Chemistry should be reflected in a detailed QA Manual as currently available for the Microbiology Certification Program. Also, for this update it is recommended that the laboratory consider the sections required by the National Environmental Laboratory Accreditation Conference/Program (NELAC) for a Quality Manual. The WVLCP certification manual for micriobiology already is pattern after NELAC. NELAC is an established program with consensus agreement of over 40 states and NELAC standards are consistent with international requirements for certifications of environmental laboratories, e.g., ISO 25. Information necessary for the WVLCP to apply to have its SDWA laboratory certification program approved by NELAC is available in Chapter 6, Accreditation Authorities, of the NELAC standard and the details are available on the NELAC web site at www.epa.gov\ttn\nelac. Whether WV decides to actually become an Accreditation Authority and offer Lab NELAC Accreditation or not, the

Freedom_0006095_0018

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL SCIENCE CENTER
701 MAPES ROAD
FORT MEADE, MD 20755-5350

June 8, 2000

Andrea M. Labik, Sc. D.
Director
West Virginia Department of Health & Human Resources
Office of Laboratory Services
Environmental Chemistry Laboratory
Charleston, West Virginia

Re: Follow-up to the May 14, 2000 report entitled "Response to EPA's Comments on West Virginia's Corrective Action Plan Relative to the Laboratory Evaluation Report (SDWA) Resulting from the On-Site Evaluation By EPA Region III Evaluators" (Inorganic Chemistry) and Follow-up to the May 14, 2000 report entitled , "Response to EPA's Comments on West Virginia's Corrective Action Plan, Relative to the SDWA Lab Certification Program Resulting from the On-Site Evaluation by EPA Region III Evaluators".

Dear Dr. Labik:

Thank you for the follow-up response to items not fully addressed by the correction actions planned relative to the on-site SDWA assessment. We hope that you will continue to pursue your plans and efforts to bring your laboratory facilities Internet access. The continued lack of E-Mail at "Big Chimney" continues to slow communications concerning inorganic chemical analyses and SDWA certification program (chemistry).

Dr. David Russell is working with Tom Ong to close out the remaining microbiology issues and will be providing a close out letter in the near future.

We understand that Charlotte Billingsley is back working part time. Great News! Please convey are well wishes.

Inorganic Chemistry:

All of the inspection findings have been addressed and the assessors agree with the corrective actions. However, relative to the purchase of PT samples for fluoride and other anions (planned for May 15th) , the assessors request that you provide a projected date when the PT study results would be forwarded to EPA.

With regard to the issue of drinking water samples which are not properly preserved or which exceed the required holding time, further discussions with our Region 3, Water Protection Division Program Office (Office of Municipal Assistance) has provided the following resolution of this issue: The laboratory is to flag (label) the analytical results for drinking water samples which are not properly preserved or do not meet the technical holding times with "Not Valid for SDWA Compliance Reporting". Based upon this approach, we recommend that the certification status for Turbidity and Conductance be upgraded to "Fully Certified" and that sulfate and TDS be upgraded to fully "acceptable" (secondary analytes).

Certification Status: The assessors recommend the following SDWA certification status based upon the November 30, 1999 on-site laboratory inspection and the resulting corrective actions:

Certified:

Arsenic; Antimony; Barium; Beryllium; Cadmium; Chromium; Copper; Lead; Mercury; Selenium; Sodium; Thallium; Nitrite; Nitrate, Fluoride, Turbidity, Conductance.

Secondary Analytes:

Acceptable: Chloride, Sulfate and TDS.

SDWA Laboratory Certification Program: All of the suggestions to improve the program resulting from the December 1, 1999 review have been implemented. Please thank your Certification Officers for their efforts.

Inspectors:

6/8/00 6/8/00
Joseph Slayton Date

6/8/00 6·8·00
Robin Costas Date

Sincerely,

Joseph Slayton
Associated Director of Science

cc: Charles Jones, Jr. (3ES10)
Jason Gambatese (3WP22)
Richard Rogers (3WP22)

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

1999

	Analyte	Instrument Detection Limit		Method Detection Limit			Linear Dynamic Range		Instrument
		Test Date	Calculated	Test Date	Fortified Reagent Water Level	Calculated	Test Date	Calculated	
2W	Aluminum	2-9-98	1.86 ppb	6-30-98	3.00 ppb	1.25 ppb	12-11-98	40.0 ppb	Varian GFAA
2W	Antimony	5-15-98	0.42 ppb	9-21-98	0.90 ppb	0.52 ppb	9-22-98	100.0 ppb	Varian GFAA
2W	Arsenic	3-16-98	0.53 ppb	12-7-98	1.06 ppb	0.81 ppb	12-7-98	40.0 ppb	Varian GFAA
2W	Barium	3-9-98	0.000232 ppm	4-16-99	0.00039 ppm	0.000135 ppm	11-4-99	10.0 ppm	Varian ICP
2W	Beryllium	5-11-98	0.03 ppb	9-30-98	0.06 ppb	0.04 ppb	9-30-98	6.00 ppb	Varian GFAA
2W	Boron								
2W	Cadmium	5-8-98	0.10 ppb	7-31-98	0.20 ppb	0.04 ppb	10-1-98	6.00 ppb	Varian GFAA
2W	Chromium	3-4-98	0.29 ppb	8-3-98	0.60 ppb	0.11 ppb	10-1-98	40.0 ppb	Varian GFAA
2W	Copper	2-9-98	0.12 ppb	6-24-98	0.30 ppb	0.19 ppb	10-1-98	20.0 ppb	Varian GFAA
2W	Iron	2-19-98	0.02 ppm	6-12-98	0.04 ppm	0.013 ppm	12-8-98	3.00 ppm	Varian AA Flame
2W	Lead	2-9-98	0.61 ppb	6-17-98	1.25 ppb	0.49 ppb	10-1-98	20.0 ppb	Varian GFAA
2W	Magnesium	8-17-99	0.000468 ppm						
2W	Manganese	2-27-98	0.017 ppm	6-12-98	0.035 ppm	0.006 ppm	12-11-98	3.00 ppm	Varian AA Flame
	Mercury	3-10-99	0.049 ppb	3-16-99	0.098 ppb	0.311 ppb	4-18-96	6.00 ppb	PE 50B Cold Vapor
	Molybdenum								
2W	Nickel	5-11-98	0.69 ppb	7-31-98	1.40 ppb	0.71 ppb	10-2-98	50.0 ppb	Varian GFAA
2W	Selenium	5-13-98	0.40 ppb	12-4-98	0.80 ppb	0.30 ppb	12-4-98	40.0 ppb	Varian GFAA
	Silver								
2W	Sodium	2-27-98	0.07 ppm	6-12-98	0.15 ppm	0.08 ppm	12-10-98	70.0 ppm	Varian AA Flame
2W	Thallium	8-12-98	0.508 ppb	8-13-98	1.00 ppb	0.391 ppb	8-13-98	30.0 ppb	PE 5100 GFAA
2W	Zinc	3-24-98	0.004 ppm	7-27-98	0.008 ppm	0.011 ppm	12-18-98	0.80 ppm	Varian AA Flame
	Calcium								
2W	Potassium	12-2-98	0.277 ppm						

1999

ML 3.8 x MDL

Analyte	Instrument Detection Limit: Test Date (CIV)	Instrument Detection Limit: Calculated (LDR)	Method Detection Limit: Test Date	Method Detection Limit: Fortified Reagent Water Level	Method Detection Limit: Calculated	Linear Dynamic Range: Test Date (MCI)	Linear Dynamic Range: Calculated (RL ISF)		Instrument
Aluminum			6-28-99	3.00 ppb	1.15 ppb				Varian GFAA
Antimony	12	100	9-13-99	0.90 ppb	0.46 ppb	6	3	4.5	Varian GFAA
Arsenic	20	40			.81	50	2	.8	
Barium	4-13-99 10000	0.000193 10000 ppm	4-16-99	0.00039	0.000135 ppm	2000	5	14	Varian ICP
Beryllium	2	6	9-1-99	0.06 ppb	0.04 ppb	4	.2	.8	Varian GFAA
Boron									
Cadmium	4	6	8-3-99	0.20 ppb	0.07 ppb	5	1	1.6	Varian GFAA
Chromium	10	40	8-3-99	0.60 ppb	0.37 ppb	100	1	4	Varian GFAA
Copper	10	20	6-25-99	0.30 ppb	0.16 ppb	1300	1	4	Varian GFAA
Iron			6-29-99	0.04 ppm	0.010 ppm				Varian AA Flame
Lead	10	20	6-24-99	1.25 ppb	0.86 ppb	15	1	4	Varian GFAA
Magnesium									
Manganese			6-29-99	0.035 ppm	0.013 ppm				Varian AA Flame
Mercury	2	6	9-21-99	0.098 ppb	0.065 ppb	2	.2	-	PE 50B Cold Vapor
Molybdenum									
Nickel	? 20	50	8-2-99	1.40 ppb	1.11 ppb	-	2	6	Varian GFAA
Selenium	10	40			.30	50	2	4	
Silver									
Sodium	100000	70000	6-29-99	0.15 ppm	0.07 ppm	2000	2000	-	Varian AA Flame
Thallium	8	30	9-14-99	1.00 ppb	0.65 ppb	-2	1	2	PE 5100 GFAA
Zinc			7-30-99	0.008 ppm	0.002 ppm				Varian AA Flame
Calcium									
Potassium									

Post-it® brand

Fax Transmittal Memo 7672

No. of Pages 15	Today's Date 3-29-00	Time	
To Joseph Slayton		From Wayne Morganroth	
Company EPA - Region III, OASQA		Company WV DHHR, Off P. H., Env. Chemistry Lab	
Location Ft. Meade, Md.		Location Charleston, WV	Dept. Charge
Fax # 1-410-305-3095	Telephone #	Fax # 1-304-558-4143	Telephone #
Comments Copy of Corrective Action Plan to 11-30-99		Original Disposition: ☐ Destroy ☐ Return ☐ Call for pickup	

through 12-2-99 on-site inspection evaluation.

3/30/00

Robin C

1999

Ex. 5 - Deliberative

CORRECTIVE ACTION PLAN

IN

RESPONSE

TO

LABORATORY EVALUATION REPORT

(SDWA)

ON-SITE EVALUATION

November 30 – December 1, 1999

BY

Office of Analytical Services and Quality Assurance

FROM

WEST VIRGINIA DEPARTAMENT OF HEALTH & HUMAN RESOURCES

OFFICE OF LABORATORY SERVICES

ENVIRONMENTAL CHEMISTRY LABORATORY

CHARLESTON, WEST VIRGINIA

Inorganic Chemistry

H. Analytical Deviations:

METALS ANALYSES

ICP Analyses:

5. All samples prepared for ICP analysis must be digested as according to method, ie., the addition of 2 mL (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid. This would translate into 700uL of nitric acid and 350 uL of hydrochloric acid per 35 mL of sample (EPA94, 200.7, 11.2.3).

Response:

The ICP method EPA94, 200.7, calls for a purposeful matrix mismatch between standards and digested samples with twice as much HCl in the standards. No explanation is given in the method nor was one given during the inspection. Our lab has been adding the same amount of acids to samples as standards to effect a 2% + 2% acid matrix (nitric + hydrochloric) to obviate any problems from trace contaminants and/or physical interferences as described in paragraph 4.2 of the method. We will, however, comply with the method per your order and make digested samples have a 2% + 1% (nitric + hydrochloric) acid matrix. We would appreciate, also, an explanation as to why this method requires a mismatching of acid matrices, as it seems to make no sense from a purely chemical standpoint.

I. Recommendations:

METALS ANALYSES

g. No value which falls below the calculated MDL should be used in any quality control ccalculations, ie., do not use these numbers to calculate the Percent Recovery for the Analytical Spike. The concept is that values below the MDL are considered "non-detectable" and, therefore, are not reliable for quality control purposes.

Response:

Values below MDL will no longer be used in calculating data. After

investigation, it was found that the instrument can be programmed to calculate analytical spikes without subtracting readings of unspiked samples if it is below the MDL. Also, MDLs of the elements in question (Pb, Tl, Sb, Cr) will be re-analyzed using instructions and suggestions given. If Reporting Levels need to be raised, then that will be done also.

h. According to the CLADW (page H-4, section 2.3), the Initial Demonstration of Capability (IDC) "consists of demonstrating proficiency in four areas: precision, accuracy (bias), method blank background, and method detection limit." It also suggests that labs "should maintain complete records for the IDC which include the bullet items in the Checklist." The Checklist, found on page H-15, section 2.3, describes an IDC as a "minimum of four replicates of a quality control or reference sample processed through all steps of the analytical procedure."

Response:

Our laboratory is in the process of complying with this new requirement of IDC as discussed. We are digesting a known QCS in four aliquots and analyzing for precision and accuracy. Results will be kept on file.

i. The digestion logbook should be self-explanatory and include all relevant information about the particular set of samples and the digestion procedure used.

Response:

The metals digestion logbook has been revised to reflect your suggestion. Headings now are as follows: Lab #, Digestion Type, Block Temp., Blank Digested (y/n), LFB Digested (y/n), Date Acidified, pH < 2 (y/n), Date Digested, Digestion Aliquot Volume Checked (y/n), Chemist Initials.

INORGANIC, NON-METALS

General

DEVIATION: Many of the QC acceptance/action limits for inorganic-non-metals where fixed limits. However, these criteria were not included in corresponding SOPs, e.g., correlation coefficient limit of 0.995 for NO3. The QC limits must be included in the SOP. In addition, the corrective actions to be taken when limits are exceeded should be added to the SOP. QA Plan only lists general approach, the SOP needs to list specifics, e.g., stop analysis, take corrective action to correct problem (new reagents, new calibration standards, new pump tubes, new photo multiplier or colorimeter bulb) and repeat all analysis since the last acceptable QC check, etc.

OLS RESPONSE: *Corrected as described.*

DEVIATION: Checks of sample Preservation, required by CLADW must be recorded, GLP.

OLS RESPONSE: *A pH log book is maintained for Nitrate-Nitrite analyses. Sample temperature is now recorded on a log in and holding time sheet. This laboratory only acccepts samples requested over the phone for hydrogen sulfide analyses. The zinc acetate used as a preservative in hydrogen sulfide analyses is added to a 500 ml dark nalgene bottle at the laboratory prior to shipping it to the customer.*

DEVIATION: The laboratory has a Sample Rejection Policy. The laboratory must reject samples not preserved as per CLADW, e.g., turbidity, or the data must be flagged indicated that required preservation was not employed and/or required technical holding times were not met.

OLS RESPONSE: *A notice is sent with the report that states the values are not valid for compliance monitoring when the sample is not received on ice.*

Combined Nitrate-Nitrite

DEVIATION: The SOP must be updated to reflect the current EPA methods manual cited by 40 CFR, which is entitled: Determination of Inorganic Substances in Environmental Samples, Aug 1993, EPA/600/R-93/100.

OLS RESPONSE: *The SOP is now based on EPA method 353.2 Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry, revision 2.0 August 1993 and all the quality control limits have been included.*

DEVIATION: Stock calibration solutions must be labeled with the date of preparation, analyst and expiration date. Stock solutions should not be retained more then a month unless verified to be accurate versus a newly prepared QC sample/ampule, GLP. Similarly, calibration standards are to be prepared fresh with each analytical batch of samples or the accuracy of the standards verified accurate versus a newly prepared QC sample/ampule, GLP.

West Virginia Corrective Action Report to Laboratory Evaluation Report (SDWA) On-Site Evaluation 11/30/99-12/1/99 By EPA – Region III, Office of Analytical Services and Quality Assurance

***OLS RESPONSE**: Corrected as described.*

DEVIATION: The samples for nitrate-nitrite must be checked and verified free of chlorine or dechlorinating reagent added. EPA 353.2, EPA-600/R-93-100, Aug 1993.

***OLS RESPONSE**: 50 µL of Sodium Thiosulfate (30 g/L) is added to every 50 ml of sample.*

Ion Chromatography (Fluoride, Chloride, Sulfate)

DEVIATION: Since the last Proficiency Testing sample for fluoride was "Not Acceptable" it is critically important that the laboratory purchase, analyze and forward PT results to EPA, which demonstrate "Acceptable" performance, prior to the analysis of additional compliance samples.

***OLS RESPONSE**: Ken Kirkbride a technical specialist from Dionex suggested the peak threshold be decreased and the method re-optimized to help identify the fluoride peak area correctly. Fluoride quality control samples from VHG LABS have been analyzed with a recovery of 100 ± 10 %. PE samples from ERA will be ordered by the end of April.*

DEVIATION: MDLs have not been determined for the IC analytes. MDLs are required under SDWA regulations CLADW and EPA 300.0

***OLS RESPONSE**: MDL Study will be completed within the next 2 months.*

DEVIATION: An SOP must be prepared for IC analyses, GLP.

***OLS RESPONSE**: A SOP is currently being worked on.*

DEVIATION: Samples for sulfate are not refrigerated. Compliance samples are to be transported on ice as per CLADW.

***OLS RESPONSE**: A notice is sent with the report that states the values are not valid for compliance monitoring when the sample is not received on ice.*

DEVIATION: An initial demonstration of capability is required for each analyte as per section 7.2.7 CLADW and as detailed in 300.0

***OLS RESPONSE**: In the process of being corrected as described.*

Turbidity

DEVIATION: Samples arrive without refrigeration and are held longer then 48 hours. Compliance samples must be maintained at 4°C from the time of sampling and analyzed within 48 hours, CLADW.

OLS RESPONSE: *A notice is sent with the report that states the values are not valid for compliance monitoring when the sample is not received on ice. Analyses are performed within the required time.*

DEVIATION: The SOP is dated and does not reference the current required method. The SOP must be updated to reference EPA-600/R-93-100, Aug 1993.

OLS RESPONSE: *The SOP is currently being updated to reflect EPA method 180.1 Determination of Turbidity by Nephelometry Revision 2.0 August 1993.*

DEVIATION: A reagent blank is not analyzed. A blank must be analyzed as per CLADW.

OLS RESPONSE: *Corrected as described.*

Total Dissolved Solids

DEVIATION: Samples are received without refrigeration. Compliance samples for TDS analyses must be maintained at 4°C from the time of sampling, CLADW.

OLS RESPONSE: *A notice is sent with the report that states the values are not valid for compliance monitoring when the sample is not received on ice.*

Conductance

DEIVATION: Samples are received without refrigeration. Compliance samples for conductance analyses must be maintained at 4°C from the time of sampling, CLADW.

OLS RESPONSE: *A notice is sent with the report that states the values are not valid for compliance monitoring when the sample is not received on ice.*

General Recommendations

RECOMMENDED: The SOPs are being updated to reflect changes in referenced methods, e.g., NO2-NO3, and changes in technology / method, e.g., IC. It is suggested that the format of the SOP be expanded to include the topics required for the method SOPs in the NELAC standards.

OLS RESPONSE: *The SOP for Nitrate-Nitrite, Alkalinity, Calcium Hardness, Total Hardness and Total Dissolved Solids have been updated as described. The SOPs for the remaining analytes are being working on.*

RECOMMENDED: The Nitrate-Nitrite MDL study should be repeated with the spike at or slightly above the concentration of the quantitation range.

OLS RESPONSE: *A new MDL was performed on Feb. 17, 2000 with a RFW of 0.008 mg/L NO_3.*

CORRECTIVE ACTION PLAN

IN

RESPONSE

TO

SDWA LAB CERTIFICATION PROGRAM

ON-SITE REVIEW

December 1-2, 1999

BY

Office of Analytical Services and Quality Assurance

FROM

WEST VIRGINIA DEPARTMENT OF HEALTH AND HUMAN RESOURCES

OFFICE OF LABORATORY SERVICES

ENVIRONMENTAL CHEMISTRY LABORATORY

CHARLESTON, WEST VIRGINIA

West Virginia Correctivwe Action Report to SDWA Lab Certification Program On-Site Review, 12/1/99 – 12/2/99 By EPA – Region III, Office of Analytical Services and Quality Assurance

Certification Program Documentation (and Procedures/SOPs):

It is readily apparent from an examination of the West Virginia Laboratory Certification Program for Chemistry that it suffers from a lack of defining procedures SOPs and documentation. In the next year to eighteen months a considerable amount time and effort will be expended in order to remedy most, if not all, of these inadequacies.

Obervations & Suggestions:

1. **Proficiency Testing (PT) Samples:** The WV Laboratory Certification Program (WVLCP) has not decided on the details of operating the new PT program (the EPA no longer provides PE/PT samples). The WVCLP should establish a schedule for laboratories to participate in Water Supply studies.

Response: During the on-site evaluation of our WVLCP for Chemistry I expressed our desire to set up a defining schedule in which the primary annual WS PT sample for those analytes a laboratory was seeking certification would be obtained/analyzed and the analytical results forwarded to our office for review no later than the end of the first quarter (March 31st) of each year. The "make- up" WS PT (for those analytes "missed" on the primary WS PT sample) sample would then need to be analyzed and reported to our office no later than the end of the third quarter (September 30th) of each year.

Since then I have decided that it would be better for our program if the "make up" PT termination date were to be set at the end of August each year rather than the end of September. This would allow more time for the recording of all PT results data (presently a time-consuming process) on each certified laboratory's index card and for an in-depth analysis of their certification status. This would materially simplify the process of sending out renewal notices/invoices by our usual target date of mid-October each year.

Such a schedule for our PT program will be documented in a written SOP covering the topics detailed in your **Observations & Suggestions.** ***A letter detailing the substance of this SOP will be drafted and forwarded (by registered or certifed mail) to all certified labs.***

2. On-Site Laboratory Inspections:

The WVCLP should maintain a record which lists the dates of inspections, analytes/analyte groups reviewed, certification status and the target/projected/estimated date (at least quarter) for the next on-site.

West Virginia Correctivwe Action Report to SDWA Lab Certification Program On-Site Review, 12/1/99 – 12/2/99 By EPA – Region III, Office of Analytical Services and Quality Assurance

Response: Implementation of this recommended procedure will begin with this year's on-site examinations.

We now have ten in-state laboratories to audit. The initiation of a program that will more evenly spread out these on-sites for each year (over a three year period) will also be put in place this year, 2000 (instead of inspecting all ten this year). In order to do this it is anticipated that there will be four on-sites in 2000, four in 2001 and three in 2002 (one and possibly two of our certified labs will be audited every other year for a presently indefinite period of time). Records of these scheduled on-sites will be recorded as detailed in your discussion of this section.

4. Documentation:

The documentation for the Microbiology Certification Program was complete and well organized. The Chemistry Certification Program lacked written procedures for Lab Certification (as detailed above for Microbiology). It is suggested that an SOP/QA Manual for the drinking water laboratory certification chemistry program be prepared.

Response: Although it is probably not as extensive or complete as that for the Microbiology Certification Program the Chemistry Certification Program does have an SOP/QA manual for drinking water laboratory certification. This manual is titled Laboratory Certification Standard Operating Procedure for West Virginia Bureau of Public Health, Office of Laboratory Service – SDWA Lab Certification Program. A copy of the Title page and the Table of Contents has been included for your examination. This manual is badly in need of being up-dated. We have some standard letters and methods check-lists in place that really should be included in this manual.

5. Personnel:

Given that Dr. Morganroth alone can certify laboratories to perform organic analyses in West Virginia, it is critically important to the WV Laboratory Certification Program to assure that Mr. Larry Duffield and Mr. Greg Young are approved as Certification Officers for organic chemistry, as well as inorganic chemistry as soon as possible.

Response: Mr. Larry Duffield's name (and additional, requested information) has been sent to Charles Jones (Region III – Philadelphia, PA) as an applicant for the Certification Officer training to be given in Cincinnati in September, 2000. This year he will be seeking certification only in the area of inorganic chemistry, however, he has verbally informed me that he would attend in 2001 for certification in the area of organic chemistry. In addition Mr. Greg Young has informed me that he would also

West Virginia Correctivwe Action Report to SDWA Lab Certification Program On-Site Review, 12/1/99 – 12/2/99 By EPA – Region III, Office of Analytical Services and Quality Assurance

attend a certification officers training course (for certification in the area of inorganic chemistry). This will be implemented as soon as it is practicable.

6. NELAC:

As described previously, the WV's Laboratory Certification Program for Chemistry should be reflected in a detailed QA Manual as currently available for the Microbiology Certification Program. Also, for this update it is recommended that the laboratory consider the sections required by the National Environmental Laboratory Accreditation Conference/Program (NELAC) for a Quality Manual.

Response: Once the NELAC document referred to is secured work will begin on the development of a detailed and more satisfactory Quality Manual.

Additional Response to On-Site Laboratory Report (SDWA) Deviation.

H. Analytical Deviations:

General:

1. The principle WV SDWA laboratory must maintain capability and certification for all the contaminants specified in the State Primary Drinking Water Regulation, p. E-1, CLADW, unless the State has been granted wavers for compliance monitoring of these analytes or has contracted with laboratories which are SDWA certified (by EPA or by a state other than WV) for these analytes. A listing of commercial laboratories employed by the State for SDWA compliance monitoring for the analytes not measured at the WV Lab and their current SDWA Certification status (State in which they hold certification, method and analytes) is necessary to complete our records.

Response: This deviation is addressed here, rather than by an analyst, since it lies more in the realm of certification than it does in that of analytical work. A copy of the listing of commercial laboratories you are requesting can be provided at a later date. This "later date" should be no more than two to four weeks. We are in the process of developing a current listing of all laboratories that are certified by West Virginia to perform drinking water analyses under the SDWA. This should be completed shortly, however, this listing does not give the home state in which out-of-state laboratories are cerjtified, nor does it give the methods used for analyzing for the various analytes. The listing does give the address of all the laboratories on the list and the analytes or

West Virginia Correctivwe Action Report to SDWA Lab Certification Program On-Site Review, 12/1/99 – 12/2/99 By EPA – Region III, Office of Analytical Services and Quality Assurance

groupings for which they are certified by West Virginia. As soon as this additional information can be compiled with our usual listing of certified laboratories it will be forwarded to your address/attention.

LABORATORY CERTIFICATION

STANDARD OPERATING PROCEDURE

FOR

WEST VIRGINIA BUREAU OF PUBLIC HEALTH
OFFICE OF LAB SERVICES

SDWA LAB CERTIFICATION PROGRAM

2/95
BJB

TABLE OF CONTENTS

SECTION I
CRITERIA FOR CERTIFYING LABORATORIES
GENERAL DIRECTIONS
GENERAL INFORMATION
OUT-OF-STATE LABORATORIES
IN-STATE LABORATORIES

SECTION II
CRITERIA FOR CERTIFYING LABORATORIES BY PARAMETER GROUPINGS
TRACE METALS
GROUP I
GROUP II
INORGANICS
GROUP I
GROUP II
GROUP III
GROUP IV
GROUP V
ORGANICS, PESTICIDES
GROUP I
GROUP II
GROUP III
GROUP IV
GROUP V
GROUP VI
GROUP VII
ORGANICS, HERBICIDES
ORGANICS, TRIHALOMETHANES
ORGANICS, VOC's
GROUP I
GROUP II
ORGANICS, SOC's
GROUP I
GROUP II
GROUP III

SECTION III
APPENDIX
A-1: TABLE OF ANALYTE GROUPINGS THAT WEST VIRGINIA CERTIFIES FOR:
A-2: CHAPTER 64 OF WV STATE REGULATIONS 3-13
A-3: GUIDELINES FOR ASBESTOS CERTIFICATION AS PRESENTED TO REGION III

A-4: GUIDELINES FOR: THIRD-PARTY CERTIFICATION FOR LABORATORIES IN PRIMACY STATES (FROM OFFICE OF DRINKING WATER {WH-550A})
B-1: APPLICATION FOR CERTIFICATION BY OUT-OF-STATE LABORATORY
C-1: EXAMPLE OF INDEX CARD USED TO TABULATE A LABORATORY'S ON-GOING PE RESULTS
D-1: INVOICE FOR LABORATORY CERTIFICATION FEES
E-1: EXAMPLE OF WV CERTIFICATE
E-2: EXAMPLE OF LABORATORY'S "CERTIFIED FOR" PARAMETERS
F-1: COPY OF A LISTING OF WV CERTIFIED LABORATORIES (1999)
F-2: FORM USED TO INDICATE A LABORATORY'S CERTIFICATION STATUS WITH REGARD TO PE RESULTS
G-1: IN-STATE LABORATORY PRE-SURVEY APPLICATION PACKET

SECTION IV

EPA MANUAL FOR THE CERTIFICATION OF LABORATORIES ANALYZING DRINKING WATER - FOURTH EDITION

State Laboratory Pre-Survey Package:

I. General Information

II. Personnel

III. Analytical A/QC

IV. A. SDWA- (Sample Containers, Preservation and Maximum Holding Times)

IV. B. SDWA- (Chemical Methodologies)

V. SDWA- (Microbiology Checklists): Please Complete and Return with Pre-Survey Package)

VI. A. NPDES (Sample Containers, Preservation and Maximum Holding Times)

VI. B. NPDES (Chemical Methodologies)

VII. NPDES (Microbiology Checklist): Please Complete and Return With Pre-Survey Package

VIII. Ambient Monitoring (Rivers, Bays, etc.) -Done under Grants to EPA (Sample Containers, Preservation and Maximum Holding Times)
ONLY COMPLETE SHOWING ANY DIFFERENCES FROM NPDES

IX. Ambient Monitoring (Rivers, Bays, etc.) -Done Under Grants to EPA (Chemical Methodologies)
ONLY COMPLETE SHOWING ANY DIFFERENCES FROM NPDES

X. Ambient Monitoring (Rivers, Bays, etc.) -Done Under Grants to EPA
ONLY COMPLETE SHOWING ANY DIFFERENCES FROM NPDES

State Laboratory Pre-Survey Package:

I. General Information

II. Personnel

III. Analytical QA/QC

IV.A SDWA- (Sample Containers, Preservation and Maximum Holding Times)

IV.B SDWA- (Chemical Methodologies)

V. SDWA (Microbiology Checklist): Please Complete and Return With Pre-Survey Package

State Laboratory SDWA and NPDES Pre-Survey Package

Date: 7/7/99

I. General Information

A. Name of Laboratory: WV Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services

B. Address: 167 11th Avenue
South Charleston, WV 25303

C. Telephone Number: (304) 558-3530

D. Name of Laboratory Director: Frank W. Lambert, Jr., Dr. P.H.

E. Provide an organizational chart of the laboratory, including any field operations or other internal affiliations to show how the laboratory fits into the general organizational structure.
Indicate SDWA and NPDES related portions of the laboratory organization.

F. List names of principal users of services of the laboratory.

Public Water Supplies	Private Individuals
County Health Departments	Bottled Water Companies
State Sanitarians & Engineers	
Private Contractors	

G. List laboratory support provided by commercial laboratories, and other State or Federal laboratories.

G. Are records maintained of problems and corrective actions?

	SDWA Y/N	NPDES Y/N
Out of control duplicate results		
Out of control spike results		
Out of control check standards		
Out of control in-house audits		

H. Are instrument calibration data recorded?

Does standard calibration include ≥3 standards and a reagent blank?

Is one calibration standard at or below the MCL (SDWA), permit limit (NPDES)?

Do standard concentrations bracket sample concentrations?

	SDWA Y/N	NPDES Y/N
Are instrument calibration data recorded?		
Does standard calibration include ≥3 standards and a reagent blank?		
Is one calibration standard at or below the MCL (SDWA), permit limit (NPDES)?		
Do standard concentrations bracket sample concentrations?		

List analyses for which "No" applies:

SDWA:

NPDES:

I. Are routine service checks performed on analytical instruments, (balances/spectrophotometers etc.)?

Is the laboratory pure water quality monitored routinely?

	SDWA Y/N	NPDES Y/N
Are routine service checks performed on analytical instruments, (balances/spectrophotometers etc.)?	Y	
Is the laboratory pure water quality monitored routinely?	Y	

Who is responsible?

SDWA (Name): Everyone in the Env. Micro Section

NPDES (Name): _____

J. Are all analytical records necessary to reconstruct the analyses maintained for 3 years?

Are calculations checked by a second analyst/supervisor?

	SDWA Y/N	NPDES Y/N
Are all analytical records necessary to reconstruct the analyses maintained for 3 years?	Y	
Are calculations checked by a second analyst/supervisor?	Y	

III. (QA and QC)

	SDWA Y/N	NPDES Y/N
K. Does your laboratory have a chain-of-custody program?	Y	
L. Are records maintained of preservation checks (verification of preservation by lab personnel)?		

Who provides the preservatives?

NPDES: _____

SDWA: _____

	SDWA Y/N	NPDES Y/N
M. Is there a sample custodian?	N*	

Name (SDWA): _____

Name (NPDES): _____

*None for Micro

N. Who is responsible for Sampling?

(SDWA): Organization: Water Plant Operators, District Engineers

Official: County Sanitarians

Phone No.: _____

(NPDES): Organization: _____

Official: _____

Phone No.: _____

	SDWA Y/N	NPDES Y/N
O. Is there a written policy for field equipment calibration and maintenance?		
P. Are records maintained of field equipment calibration and maintenance?		
Q. Does the laboratory have a written sample rejection policy?		
R. Do samples arrive on ice?	N*	

*for Micro

State Laboratory Pre-Survey Package:

I. General Information

II. Personnel

III. Analytical QA/QC

IV.A SDWA- (Sample Containers, Preservation and Maximum Holding Times)

IV.B SDWA- (Chemical Methodologies)

V. SDWA (Microbiology Checklist): Please Complete and Return With Pre-Survey Package

I. General Information

State Laboratory SDWA and NPDES Pre-Survey Package

Date: September 13, 1999

I. General Information

A. Name of Laboratory: WV Bureau for Public Health, Office of Lab Services
Environmental Chemistry Laboratory Section

B. Address: 4710 Chimney Drive, Suite G
Charleston, West Virginia 25302

C. Telephone Number: 1-304-558-0197

D. Name of Laboratory Director: Dr. Frank W. Lambert, Jr., (Dir O.L.S.)

E. Provide an organizational chart of the laboratory, including any field operations or other internal affiliations to show how the laboratory fits into the general organizational structure.
Indicate SDWA and NPDES related portions of the laboratory organization.

F. List names of principal users of services of the laboratory.

WV Office of Environmental Health Services Engineering Division Field Engineers, County Health Department Sanitarians, Public Water Systems and private citizens.

G. List laboratory support provided by commercial laboratories, and other State or Federal laboratories.

Perform analyses for Public Water Systems, some analyses for Field Engineers that our laboratory cannot perform and private citizens. Any analyses for organic parameters are provided by commercial laboratories.

Personnel

WV Bureau for Public Health
Lab Name Office of Lab Services - Microbiology

Please complete this chart for all technical personnel, including the laboratory director. Use a separate block for each employee and arrange the presentation to reflect the lines of organizational responsibility.

Date 7/7/99 No. ____ of ____ pages

Name	Training: Degree (Circle One)	Training: Major	Position	Years of Experience: Present Job	Years of Experience: Previous Job	Identify Current Analyses Performed in Support of: SDWA	Identify Current Analyses Performed in Support of: NPDES
Micah Moore	Ph.D. MS BS/BA Assoc. HS	Chemistry	Laboratory	2 mo.		Total Coliform Fecal Coliform E coli HPC	
	Ph.D. MS BS/BA Assoc. HS						
	Ph.D. MS BS/BA Assoc. HS						
	Ph.D. MS BS/BA Assoc. HS						
	Ph.D. MS BS/BA Assoc. HS						
	Ph.D. MS BS/BA Assoc. HS						

STATE LABORATORY PRE-SURVEY PACKAGE

I. GENERAL INFORMATION

II. PERSONNEL

III. ANALYTICAL QA/QC

IV.

A. SDWA (Sample Containers, Preservation and Maximum Holding Times).

B. SDWA (Chemical Methodologies)

V. SDWA (Microbiology Checklist): Please complete and return with pre-survey package.

H. Indicate the approximate number of samples analyzed:

	Approximate number of Samples/Year	Approximate % of Laboratory Workload/Yr
SDWA:	588 (Average of the last 2 fiscal years)	
NPDES:		
RCRA:		
Superfund:		
Other Monitoring:		

Personnel

WV Bur for Public Health
~~Office of Lab Services~~
Lab Name Environmental Chem. Laboratory

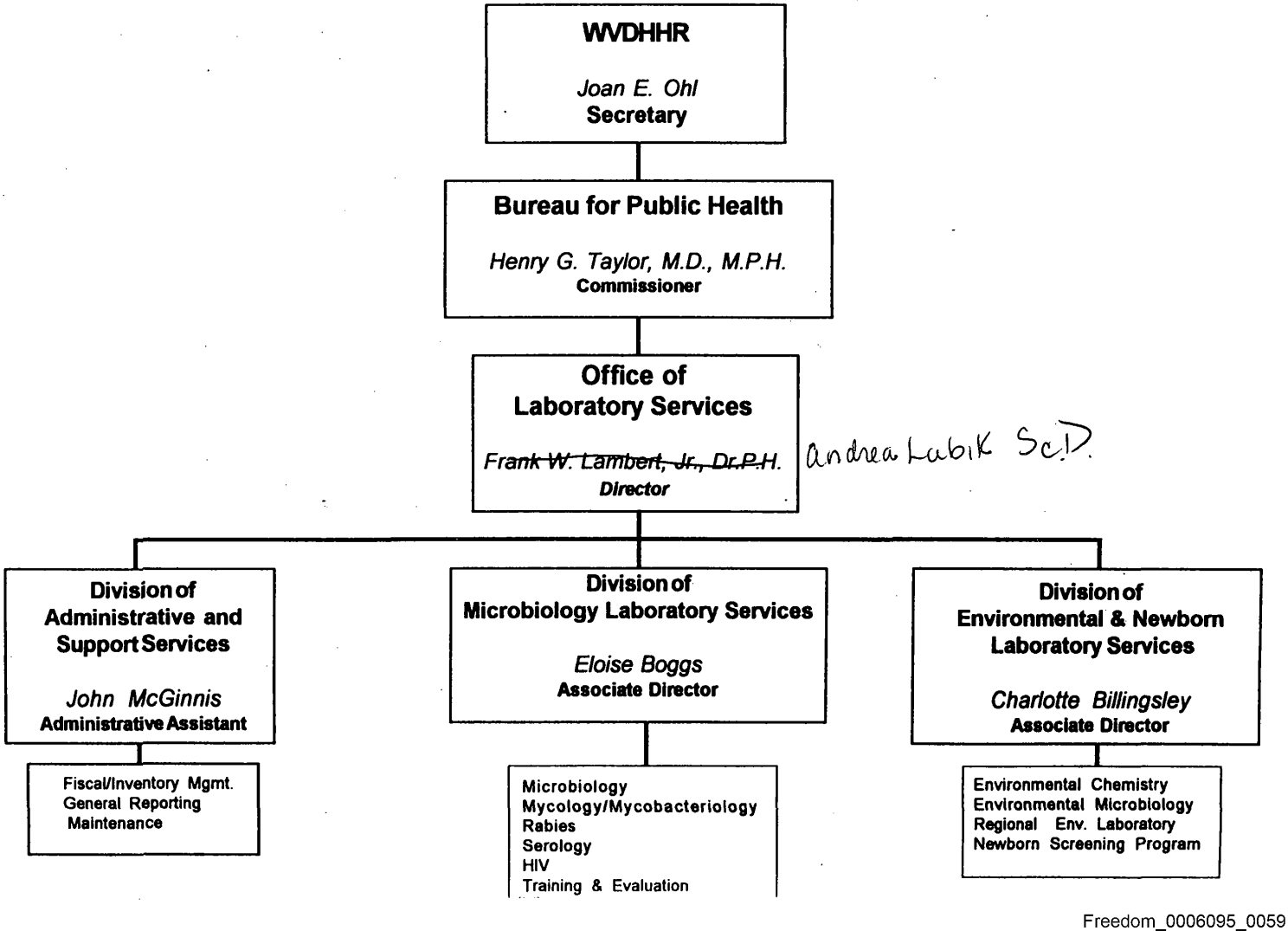
Please complete this chart for all technical personnel, including the laboratory director. Use a separate block for each employee and arrange the presentation to reflect the lines of organizational responsibility.

Date September 13, 1999 No. 1 of 1 pages

Name	Training: Degree (Circle One)	Training: Major	Position	Years of Experience: Present Job	Years of Experience: Previous Job	Identify Current Analyses Performed in Support of: SDWA	Identify Current Analyses Performed in Support of: NPDES
~~Frank W. Lambert, Jr.~~ Andrea Labaik SCd	Ph.D. MS BS/BA Assoc. HS			started Oct 1999			
Wayne Morganroth	Ph.D. MS BS/BA Assoc. HS	Chemistry	Lab. Sup.	5 yrs 11 mos.	4 Years		
Larry A. Duffield	Ph.D. MS BS/BA Assoc. HS	Biology	Chemist II	15 years	5 years	Metals analyses Flame & GFAA AA and ICP AES analytical work	Does inspections too
Greg W. Young	Ph.D. MS BS/BA Assoc. HS	Chemistry	Chemist I	7 Months	2 Yrs 7 mos.	Nitrate, Nitrite pH, Cond., Chloride, Alk., TDS, Hardness Sulfate, Fluoride Turb.	
	Ph.D. MS BS/BA Assoc. HS						
	Ph.D. MS BS/BA Assoc.						

SEP 15 '99 08:58 ENVIRONMENTAL CHEM LAB 304 558 4143 P.5/5

West Virginia Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services



III. (QA and QC)

	SDWA Y/N	NPDES Y/N
A. Is there a written Quality Control Program plan?	Y* N	
B. Is there a Quality Assurance Manual?	Y	
C. Is there a Quality Control Officer?	Y	

* No individual plan - included as a part of analytical procedures.

Name (SDWA): Wayne Morganroth

Name (NPDES): _____

D. Frequency of:

	SDWA	NPDES
Duplicate Analyses? For primary metals & inorganics	10%	
Spike Analyses? All metals samples and one per analytical run for inorganics (primary analytes)	Y	
Check Standards: 10% of metals and primary inorganic analytes.	Y	
In-House Audits?	N	

E. Records and Control Limits Maintained:

	SDWA Records Y/N	SDWA Limits Y/N	NPDES Records Y/N	NPDES Limits Y/N
Duplicate Analyses?	Y	Y		
Spike Analyses?	Y	Y		
Check Standards?	Y	Y		

For primary and secondary metals - is being implemented for primary inorganics.

List analyses for which "No" applies

SDWA:

NPDES:

F. How are the QC analyses used?

Duplicate analyses (SDWA): to determine the degree of analytical precision

Duplicate Analyses (NPDES): _____

Spike Analyses (SDWA): to assess the degree of analyte recovery

Spike Analyses (NPDES): _____

Check Standards: determine calibration stability and analytical validity.

III. (QA and QC)

	SDWA Y/N	NPDES Y/N
G. Are records maintained of problems and corrective actions?		
Out of control duplicate results	N*	
Out of control spike results	N*	
Out of control check standards	N*	
Out of control in-house audits	NA	

If data is out of control the procedure is examined for problems and repeated to obtain satisfactory results.

	SDWA Y/N	NPDES Y/N
H. Are instrument calibration data recorded?	Y	
Does standard calibration include ≥3 standards and a reagent blank?	Y	
Is one calibration standard at or below the MCL (SDWA), permit limit (NPDES)?	Y	
Do standard concentrations bracket sample concentrations?	Y	

List analyses for which "No" applies:

SDWA: Analyses for Secondary and miscellaneous inorganic non-metal contaminants.

NPDES:

	SDWA Y/N	NPDES Y/N
I. Are routine service checks performed on analytical instruments, (balances/spectrophotometers etc.)?	Y	
Is the laboratory pure water quality monitored routinely?	Y	

Who is responsible?

SDWA (Name): Metals lab: Larry Duffield
Inorganic non-metals lab: Greg Young

NPDES (Name): _____

	SDWA Y/N	NPDES Y/N
J. Are all analytical records necessary to reconstruct the analyses maintained for 3 years?	Y	
Are calculations checked by a second analyst/ supervisor?	N*	

* Being implemented.

III. (QA and QC)

	SDWA Y/N	NPDES Y/N
K. Does your laboratory have a chain-of-custody program?	Y	
L. Are records maintained of preservation checks (verification of preservation by lab personnel)?	Y	

Who provides the preservatives?

NPDES: _____

SDWA: Our laboratory.

	SDWA Y/N	NPDES Y/N
M. Is there a sample custodian?	Y	

Name (SDWA): Wayne Morganroth

Name (NPDES): _____

N. Who is responsible for Sampling?

(SDWA): Organization: Our laboratory (mailed sampling instructions), WV State Health Dept., District Engineers, county sanitarians, and customers.

Official: For our lab: Wayne Morganroth

Phone No.: 1-304-558-0197

(NPDES): Organization: _____

Official: _____

Phone No.: _____

	SDWA Y/N	NPDES Y/N
O. Is there a written policy for field equipment calibration and maintenance?	NA	
P. Are records maintained of field equipment calibration and maintenance?	NA	
Q. Does the laboratory have a written sample rejection policy?	Y	
R. Do samples arrive on ice?	Y*	

* For those samples we supply sampling supplies and instructions.

SDWA (Circle or Explain)

Hardness?

IV A. **Preservation and Holding Times for Regulated Parameters**

Parameter/ Method	Preservative	Sample Holding Time	Extract Holding Time	Suggested Sample Size	Type of Container
Metals (except Hg)	HNO_3 pH<2	6 months		1 L	Plastic or Glass
Mercury	HNO_3 pH<2	28 days		~~100 mL~~ 1 L	Plastic or Glass
Alkalinity	Cool, 4C *	14 days		~~100 mL~~ 1 L	Plastic or Glass
Asbestos	Cool, 4C	48 hours			Plastic or Glass
Chloride	none	28 days		~~50 mL~~ 1 L	Plastic or Glass
Residual Disinfectant	none	immediately		200 mL	Plastic or Glass
Color	Cool, 4C	48 hours		50 mL	Plastic or Glass
Conductivity	Cool, 4C *	28 days		~~100 mL~~ 1 L	Plastic or Glass
Cyanide	Cool, 4C, Ascorbic acid (if chlorinated), NaOH pH>12	14 days		1 L	Plastic or Glass
Fluoride	none	28 days		~~300 mL~~ 500 ml	Plastic or Glass
Foaming Agents	Cool, 4C	48 hours			
Nitrate (chlorinated)	Cool, 4C	28 days		100 mL	Plastic or Glass
Nitrate (non chlorinated)	Cool, 4C, H_2SO_4, pH<2	14 days		100 mL	Plastic or Glass
Nitrite	Cool, 4C	48 hours		~~50 mL~~ 100 ml	Plastic or Glass
Odor	Cool, 4C	24 hours		200 mL	Glass
pH	none	immediately +		~~25 mL~~ 1 L	Plastic or Glass
o-Phosphate	Filter immediately, Cool, 4C	48 hours		50 mL	Plastic or Glass
Silica	Cool, 4C	28 days		100 mL	Plastic
Solids (TDS)	Cool, 4C *	7 days @		~~100 mL~~ 1 L	Plastic or Glass
Sulfate	Cool, 4C *	28 days		~~50 mL~~ 1 L	Plastic or Glass

Parameter/ Method	Preservative	Sample Holding Time	Extract Holding Time	Suggested Sample Size	Type of Container
Temperature	none	immediately		1 L	Plastic or Glass
Turbidity	Cool, 4C *	48 hours **		~~100 mL~~ 1 L	Plastic or Glass
502.2	Sodium Thiosulfate or Ascorbic Acid, 4C, HCl pH<2	14 days		40-120 mL	Glass with Teflon Lined Septum
504.1	Sodium Thiosulfate Cool, 4C,	14 days	4C, 24 hours	40 mL	Glass with Teflon Lined Septum
505	Sodium Thiosulfate Cool, 4C	14 days (7 days for Heptachlor)	4C, 24 hours	40 mL	Glass with Teflon Lined Septum
506	Sodium Thiosulfate Cool, 4C, Dark	14 days	4C, dark 14 days	1 L	Amber Glass with Teflon lined Cap
507	Sodium Thiosulfate Cool, 4C, Dark	14 days(see method for exceptions)	4C, dark 14 days	1 L	Amber Glass with Teflon Lined Cap
508	Sodium Thiosulfate Cool, 4C, Dark	7 days (see method for exceptions)	4C, dark 14 days	1 L	Glass with Teflon Lined Cap
508A	Cool, 4C	14 days	30 days	1 L	Glass with Teflon Lined Cap
508.1	Sodium Sulfite HCl pH<2 Cool, 4C	14 days (see method for exceptions)	30 days	1 L	Glass with Teflon Lined Cap
515.1	Sodium Thiosulfate Cool, 4C, Dark	14 days	4C, dark 28 days	1 L	Amber Glass with Teflon Lined Cap
515.2	Sodium Thiosulfate HCl pH<2 Cool, 4C, Dark	14 days	≤4C, dark 14 days	1 L	Amber Glass with Teflon Lined Cap
524.2	Ascorbic Acid HCl pH<2, Cool 4C	14 days		40-120 mL	Glass with Teflon Lined Septum

NOTES TO ACCOMPANY SELECTIONS MADE IN PRESERVATION AND HOLDING TIMES FOR REGULATED PARAMETERS

* Samples are received (via mail, UPS, etc.) in the laboratory at ambient temperature - they are then placed in a refrigerator at 4 degrees C.

+ Since sample receipt in the laboratory is usually at least one to several days after the time of sampling, "immediate analysis" is precluded.

@ Due to the post-sampling "age" of most samples (see +, above), analyzing samples strictly within the maximum holding time period for these parameters is difficult or impossible.

** Yes if the sample is not "too old" when received in the laboratory.

SDWA (Circle or Fill in "other"

IV B. **Approved Methods for Primary Inorganic Chemicals, Parameters in the Lead and Copp Rule, Sodium, and Turbidity [§141.23(k)(1)]**

Contaminant	Methodology	EPA	ASTM[3]	SM[4]	Ot
Antimony	ICP-MS	200.8[2]			
	Hydride-AA		D3697-92		
	AA-Platform	200.9[2]			
	AA-Furnace			3113B	
Arsenic	ICP	200.7[2]		3120B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
	AA-Furnace		D2972-93C	3113B	
	Hydride-AA		D2972-93B	3114B	
Asbestos	TEM	100.1[9]			
	TEM	100.2[10]			
Barium	ICP	200.7[2]		3120B	
	ICP-MS	200.8[2]			
	AA-Direct			3111D	
	AA-Furnace			3113B	
Beryllium	ICP	200.7[2]		3120B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
	AA-Furnace		D3645-93B	3113B	
Cadmium	ICP	200.7[2]			
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
	AA-Furnace			3113B	
Chromium	ICP	200.7[2]		3120B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
	AA-Furnace			3113B	

Contaminant	Methodology	EPA	ASTM[3]	SM[4]	Other
Cyanide	Man. Distillation followed by:			4500-CN-C	
	Spec., Amenable		D2036-91B	4500-CN-G	
	Spec.Manual		D2036-91A	4500-CN-E	I-3300-85[5]
	Semi-auto	335.4[6]			
	Ion Sel. Elec.(ISE)			4500CN-F	
Fluoride	Ion Chromatography	300.0[6] #	D4327-91	4110B	
	Manual Distill. SPADNS			4500F-B,D	
	Manual ISE		D1179-93B	4500F-C	
	Automated ISE				380-75WE[11]
	Auto. Alizarin			4500F-E	129-71W[11]
Mercury	Manual Cold Vapor	245.1[2]	D3223-91	3112B	
	Auto. Cold Vapor	245.2[1]			
	ICP-MS	200.8[2]			
Nitrate	Ion Chromatography	300.0[6] #	D4327-91	4110B	B-1011[8]
	Auto Cd Reduction	353.2[6]	D3867-90A	4500-NO_3-F	
	Ion Selective Elec.			4500-NO_3-D	601[7]
	Man Cd Reduction		D3867-90B	4500-NO_3-E	
Nitrite	Ion Chromatography	300.0[6] #	D4327-91	4110B	B-1011[8]
	Auto Cd Reduction	353.2[6]	D3867-90A	4500-NO_3-F	
	Man Cd Reduction		D3867-90B	4500-NO_3-E	
	Spectrophotometric			4500-NO_2-B	
Selenium	Hydride-AA		D3859-93A	3114B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
	AA-Furnace		D3859-93B	3113B	
Thallium	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			

Contaminant	Methodology	EPA	ASTM[3]	SM[4]	Other
Lead	AA-Furnace		D3559-90D	3113B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
Copper	AA-Furnace		D1688-90C	3113B	
	AA-Direct		D1688-90A	3111B	
	ICP	200.7[2]		3120B	
	ICP-MS	200.8[2]			
	AA-Platform	200.9[2]			
pH	Electrometric	150.1[1]	D1293-84	4500-H^+-B	
		150.2[1]			
Conductivity	Conductance		D1125-91A	2510B	
Calcium	EDTA titration		D511-93A	3500-Ca-D	
	AA-Direct		D511-93B	3111B	
	ICP	200.7[2]		3120B	
Alkalinity	Titration		D1067-92B	2320B	
	Elec. titration				I-1030-85[5]
Ortho-phosphate unfiltered, no digestion or hydrolysis	Color, automated ascorbic acid	365.1[6]		4500-P-F	
	Color, ascorbic acid		D515-88A	4500-P-E	
	Color, phosphomolybdate				I-1601-85[5]
	AutoSegmented Flow				I-2601-90[5]
	Auto discrete				I-2598-85[5]
	Ion Chromatography	300.0[6]	D4327-91	4110	
Silica	Color, molybdate blue;				I-1700-85[5]
	auto seg. flow				I-2700-85[5]
	Color		D859-88		
	Molybdosilicate			4500-Si-D	
	Heteropoly blue			4500-Si-E	

Contaminant	Methodology	EPA	ASTM[3]	SM[4]	Other
	Auto. molybdate reactive silica			4500-Si F	
	ICP	200.7[2]		3120B	
Temperature	Thermometric			2550B	
Sodium	ICP	200.7[2]			
	AA-Direct			3111B	
Turbidity	Nephelometric[6]	180.1		2130B	GLI Method 2[12]

FOOTNOTES

1. Methods 150.1, 150.2 and 245.2 are available from US EPA, EMSL, Cincinnati, OH 45268. The identical methods were formerly in "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020, March 1983.
2. "Methods for the Determination of Metals in Environmental Samples - Supplement I," EPA-600/R-94-111, May 1994. Available at NTIS, PB 94-184942.
3. *Annual Book of ASTM Standards*, Vols. 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
4. *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.
5. Available from Books and Open-File Reports Section, U.S. Geological Survey, Federal Center, Box 25425, Denver, CO 80225-0425.
6. "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
7. Technical Bulletin 601 "Standard Method of Test for Nitrate in Drinking Water," July 1994, PN 221890-001, ATI Orion, 529 Main Street, Boston, MA 02129. This method is identical to Orion WeWWG/5880, which is approved for nitrate analysis. ATI Orion republished the method in 1994, and renumbered it as 601, because the 1985 manual "Orion Guide to Water and Wastewater Analysis," which contained WeWWG/5880, is no longer available.
8. Method B-1011, "Waters Test Method for Determination of Nitrite/Nitrate in Water Using Single Column Ion Chromatography," Millipore Corporation, Waters Chromatography Division, 34 Maple Street, Milford, MA 01757.
9. Method 100.1, "Analytical Method for Determination of Asbestos Fibers in Water," EPA-600/4-83-043, EPA, September 1983. Available at NTIS, PB 83-260471.
10. Method 100.2, "Determination of Asbestos Structure Over 10-μm In Length in Drinking Water," EPA-600/R-94-134, June 1994, Available at NTIS, PB 94-201902.
11. Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976, Technicon Industrial Systems, Tarrytown, NY 10591.
12. GLI Method 2, "Turbidity," November 2, 1992, Great Lakes Instruments, Inc., 8855 North 55th Street, Milwaukee, Wisconsin 53223

Table IV-6 Recommended Methods for Secondary Drinking Water Contaminants

Analyses of aluminum, chloride, color, copper, fluoride, foaming agents, iron, manganese, odor, silver, sulfate, total dissolved solids (TDS) and zinc to determine compliance under §143.3 may be conducted with the methods in the following Table. Criteria for analyzing aluminum, copper, iron, manganese, silver, and zinc samples with digestion or directly without digestion, and other mandatory procedures are contained in the Technical Notes in Section IV of this document. Measurement of pH may be conducted with one of the methods listed above in Section I under "Methods for Inorganic Chemicals."

Contaminant	EPA	ASTM[1]	SM[2]	Other
Aluminum	200.7[3]		3120B	
	200.8[3]		3113B	
	200.9[3]		3111D	
Chloride	300.0[4] #	D4327-91	4110B	
			4500-Cl-D	
Color			2120B	
Foaming Agents			5540C	
Iron	200.7[3]		3120B	
	200.9[3]		3111B	
			3113B	
Manganese	200.7[3]		3120B	
	200.8[3]		3111B	
	200.9[3]		3113B	
Odor			2150B	
Silver	200.7[3]		3120B	I-3720-85[6]
	200.8[3]		3111B	
	200,9[3]		3113B	
Sulfate	300.0[4] #	D4327-91	4110B	
	375.2[4]		4500-SO_4-F	
			4500-SO_4-C,D	
TDS			2540C	
Zinc	200.7[3]		3120B	
	200.8[3]		3111B	

"Unregulated" Inorganic Contaminants	Methods EPA	ASTM	SM
Nickel	200.7		3120B
	200.8		
	200.9		
			3111B
			3113B
Sulfate	300.0 #	D4327-91	4110B
	375.2		4500-SO_4-F
			4500-SO_4-C,D

*A Standard Methods method.

Sources for the Standard Methods and ASTM sulfate methods are referenced above under methods for inorganic chemicals. The EPA methods are contained in "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993, which is available at NTIS, PB94-121811.

NOTE REFERENCED TO EPA METHOD 300.0 IN TABLES IV B AND IV-6

 # Marking of EPA approved method 300.0 for the following parameters:

Chloride
Fluoride
Nitrate
Nitrite, and
Sulfate

signifies that our laboratory is actively in the process of switching over to ion chromatographic analysis for these analytes.

Footnotes

[1] *Annual Book of ASTM Standards*, Vols. 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
[2] *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.
[3] "Methods for the Determination of Metals in Environmental Samples - Supplement I," EPA-600/R-94-111, May 1994. Available at NTIS, PB94-184942.
[4] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
[5] Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976, Technicon Industrial Systems, Tarrytown, NY 10591.
[6] Available from Books and Open-File Reports Section, U.S. Geological Survey, Federal Center, Box 25425, Denver, CO 80225-0425.

Table IV-5. Sample Collection, Containers, and Preservation for Organic Contaminants

Contaminant	Method	Preservative	Container	Holding Time: To Extraction	Holding Time: After Extraction
Non-Volatile SOCs	504	3 mg/40 ml sodium thiosulfate HCl to pH 2 Cool 4° C	Glass Teflon cap liners	28 days	Analyze immediately
	505	3 mg/40 ml sodium thiosulfate Cool 4° C	Glass Teflon cap liners	14 days*	Analyze immediately
	506	60 mg/l sodium thiosulfate Cool 4°C	Glass(dark) Teflon cap liners	14 days	14 days
	507	10 mg/l mercuric chloride** 80 mg/l sodium thiosulfate Cool 4° C	Glass (dark) Teflon cap liners	14 days	14 days
	508A	Cool 4° C	Glass Teflon cap liners	14 days	30 days
	508	10 mg/l mercuric chloride** 80 mg/l sodium thiosulfate Cool 4° C	Glass Teflon cap liners	7 days	14 days
	515.1	10 mg/l mercuric chloride** 80 mg/l sodium thiosulfate Cool 4° C	Glass(dark) Teflon cap liners	14 days	28 days
	525.1	40-50 mg/l sodium sulfite HCl to pH < 2 Cool 4° C	Glass Teflon cap liners	7 days	30 days
	531.1	Monochloracetic acid to pH 3 80 mg/l sodium thiosulfate Cool 4° C until storage Store at -10° C	Glass Teflon cap liners	28 days at -10°C	No extract
	547	100 mg/l sodium thiosulfate Cool 4°C	Glass(dark) Teflon cap liners	14 days	No extract
	548	Cool 4°C	Glass Teflon cap liners	7 days	1 day
	549	100 mg/l sodium thiosulfate H_2SO_4 to pH 2 Cool 4°C	Amber PVC high density. or amber silanized glass	7 days	21 days
	550	100 mg/l sodium thiosulfate 6N HCL to pH < 2 Cool 4°C	Glass(dark) Teflon cap liners	7 days	40 days
	550.1	100 mg/l sodium thiosulfate 6N HCL to pH < 2 Cool 4°C	Glass (dark) Teflon cap liners	7 days	40 days
	1613	80mg/l sodium thiosulfate Cool 4°C	Glass (dark)	—	40 days
TTHMs	501.1	3 mg/40 ml sodium thiosulfate (except for MTTHM) or Sodium Sulfite	Glass Silicon/Teflon cap liners	14 days	—
	501.2	3 mg/40 ml sodium thiosulfate (except for MTTHM) or Sodium Sulfite	Glass Silicon/Teflon cap liners	14 days	—
	510.1	Cool 4° C	Glass (dark) Silicon/Teflon cap liners	14 days	—
VOCs	502.1	25 mg/40 ml ascorbic acid or 3 mg/40 ml sodium thiosulfate 1:1 HCl to pH < 2 Cool 4° C	Glass Silicon/Teflon cap liners	14 days	—
	502.2	25 mg/40 ml ascorbic acid or 3 mg/40 ml sodium thiosulfate 1:1 HCl to pH < 2 Cool 4° C	Glass Silicon/Teflon cap liners	14 days	—
	503.1	25 mg/60 ml ascorbic acid or 3 mg/40 ml sodium thiosulfate 1:1 HCl to pH < 2 Cool 4° C	Glass Silicon/Teflon cap liners	14 days	—

Indicate Yes or No for each

Table IV-5. Sample Collection, Containers, and Preservation for Organic Contaminants

Contaminant	Method	Preservative	Y/N	Container	Y/N	Holding Time: To Extraction	Y/N	Holding Time: After Extraction	Y/N
	524.1	25 mg/60 ml ascorbic acid 1:1 HCl to pH < 2 Cool 4° C		Glass Silicon/Teflon cap liners		14 days		—	
	524.2	25 mg/60 ml ascorbic acid 1:1 HCl to pH < 2 Cool 4° C		Glass Silicon/Teflon cap liners		14 days		—	

* The holding time for Heptachlor under this method is 7 days.

** Samples that have been preserved with $HgCl_2$ may be disposed of in at least two ways: as a hazardous waste, or by passing over an absorbent column (i.e., Alumina, activated with carbon, etc.) for mercury absorption, with the effluent analyzed periodically for breakthrough. The absorbent would then be disposed of as a hazardous waste. Other techniques may be applicable.

Table IV-3 Approved Methods for Primary Organic Chemicals [§141.24(e)]

Contaminant	Method[3]
Benzene	502.2, 524.2
Carbon tetrachloride	502.2, 524.2, 551
Chlorobenzene	502.2, 524.2
1,2-Dichlorobenzene	502.2, 524.2
1,4-Dichlorobenzene	502.2, 524.2
1,2-Dichloroethane	502.2, 524.2
cis-1,2-Dichloroethylene	502.2, 524.2
trans-1,2-Dichloroethylene	502.2, 524.2
Dichloromethane	502.2, 524.2
1,2-Dichloropropane	502.2, 524.2
Ethylbenzene	502.2, 524.2
Styrene	502.2, 524.2
Tetrachloroethylene	502.2, 524.2, 551
1,1,1-Trichloroethane	502.2, 524.2, 551
Trichloroethylene	502.2, 524.2, 551
Toluene	502.2, 524.2
1,2,4-Trichlorobenzene	502.2, 524.2
1,1-Dichloroethylene	502.2, 524.2
1,1,2-Trichloroethane	502.2, 524.2
Vinyl chloride	502.2, 524.2
Xylenes (total)	502.2, 524.2
2,3,7,8-TCDD (dioxin)	1613
2,4-D	515.2, 515.1, 555
Alachlor	505[1], 507, 508.1, 525.2
Atrazine	505[1], 507, 508.1, 525.2
Benzo(a)pyrene	525.2, 550, 550.1
Carbofuran	531.1, 6610
Chlordane	505, 508, 508.1, 525.2

Contaminant	Method[3]
Dalapon	515.1, 552.1
Di(2-ethylhexyl)adipate	506, 525.2
Di(2-ethylhexyl)phthalate	506, 525.2
Dibromochloropropane (DBCP)	504.1, 551
Dinoseb	515.2,515.1, 555
Diquat	549.1
Endothall	548.1
Endrin	505, 508, 508.1, 525.2
Ethylene dibromide (EDB)	504.1, 551
Glyphosate	547, 6651
Heptachlor	505, 508, 508.1, 525.2
Heptachlor Epoxide	505, 508, 508.1, 525.2
Hexachlorobenzene	505, 508, 508.1, 525.2
Hexachlorocyclopentadiene	505, 508, 508.1, 525.2
Lindane	505, 508, 508.1, 525.2
Methoxychlor	505, 508, 508.1, 525.2
Oxamyl	531.1, 6610
PCBs (as decachlorobiphenyl)[2] (as Aroclors)	508A 505, 508
Pentachlorophenol	515.1, 515.2, 525.2, 555
Picloram	515.1, 515.2, 555
Simazine	505[1], 507, 508.1, 525.2
2,4,5-TP (Silvex)	515.1, 515.2, 555
Toxaphene	505, 508, 525.2
Total Trihalomethanes	502.2, 524.2, 551

[1] A nitrogen-phosphorous detector should be substituted for the electron capture detector in Method 505 (or another approved method should be used) to determine alachlor, atrazine and simazine, if lower detection limits are required.

[2] PCBs are qualitatively identified as Aroclors and measured for compliance purposes as decachlorobiphenyl using Method 508A.

[3] Methods 502.2, 505, 507, 508, 508A, 515.1 and 531.1 are in Methods for the Determination of Organic Compounds in Drinking Water, EPA-600/4-88-039, December 1988, Revised, July 1991. Methods 506, 547, 550, 550.1 and 551 are in Methods for the Determination of Organic Compounds in Drinking Water -

Footnotes

[1] *Annual Book of ASTM Standards*, Vols. 11.01 and 11.02, American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.
[2] *Standard Methods for the Examination of Water and Wastewater*, 18th Edition, 1992, American Public Health Association, 1015 Fifteenth Street NW, Washington, D.C. 20005.
[3] "Methods for the Determination of Metals in Environmental Samples - Supplement I," EPA-600/R-94-111, May 1994. Available at NTIS, PB94-184942.
[4] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA-600/R-93-100, August 1993. Available at NTIS, PB94-121811.
[5] Industrial Method No. 129-71W, "Fluoride in Water and Wastewater," December 1972, and Method No. 380-75WE, "Fluoride in Water and Wastewater," February 1976, Technicon Industrial Systems, Tarrytown, NY 10591.
[6] Available from Books and Open-File Reports Section, U.S. Geological Survey, Federal Center, Box 25425, Denver, CO 80225-0425.

Table IV-4 Approved Methods for "Unregulated" Contaminants (§141.40)

Regulations specified in §141.40 require monitoring for certain contaminants to which maximum contaminant levels do not apply. These chemicals are called "unregulated" contaminants, and presently include sulfate, 34 volatile organic chemicals (VOCs) and 13 synthetic organic chemicals (SOCs).

Analysis for the 34 unregulated VOCs listed under paragraphs (e) and (j) of §141.40 shall be conducted using the following recommended methods, or their equivalent as determined by EPA.

"Unregulated" VOC Contaminants	Method
Chloroform	502.2, 524.2, 551
Bromodichloromethane	502.2, 524.2, 551
Bromoform	502.2, 524.2, 551
Chlorodibromomethane	502.2, 524.2, 551
Bromobenzene	502.2, 524.2
Bromomethane	502.2, 524.2
Chloroethane	502.2, 524.2
Chloromethane	502.2, 524.2
o-Chlorotoluene	502.2, 524.2
p-Chlorotoluene	502.2, 524.2
Dibromomethane	502.2, 524.2
m-Dichlorobenzene	502.2, 524.2
1,1-Dichloroethane	502.2, 524.2
1,3-Dichloropropane	502.2, 524.2
2,2-Dichloropropane	502.2, 524.2
1,1-Dichloropropene	502.2, 524.2
1,3-Dichloropropene	502.2, 524.2
1,1,2,2-Tetrachloroethane	502.2, 524.2
1,1,1,2-Tetrachloroethane	502.2, 524.2
1,2,3-Trichloropropane	502.2, 524.2, 504.1

State Discretionary Contaminants	METHODS
Bromochloromethane	502.2, 524.2
n-Butylbenzene	502.2, 524.2
sec-Butylbenzene	502.2, 524.2

Table IV-2. Approved Methodology for Organic Contaminants

Contaminant	MCL mg/l	Methodology	Reference EPA[1]
Non-Volatile SOCs			
Adipates [Di(ethylhexyl)adipate]	0.4	Gas Chromatography-Liquid/Liquid or Liquid/Solid Extraction-Photoionization Detector	506[2]
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Alachlor	0.002	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Nitrogen/Phosphorus Detector	507
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Aldicarb*	–	High Performance Liquid Chromatography-Post Column Reactor	531.1
Aldicarb sulfoxide*	–	High Performance Liquid Chromatography-Post Column Reactor	531.1
Aldicarb sulfone*	–	High Performance Liquid Chromatography-Post Column Reactor	531.1
Atrazine	0.003	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Nitrogen/Phosphorus Detector	507
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Carbofuran	0.04	High Performance Liquid Chromatography-Post Column Reactor	531.1
Chlordane	0.002	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Dalapon	0.2	Gas Chromatography-Electron Capture Detector	515.1
Dibromochloropropane(DBCP)	0.0002	Gas Chromatography-Microextraction-Electron Capture Detector	504
2,4-D	0.07	Gas Chromatography-Electron Capture Detector	515.1**
Dinoseb	0.007	Gas Chromatography-Electron Capture Detector	515.1
Diquat	0.02	High Performance Liquid Chromatography-Liquid/Solid Extraction-Ultraviolet Detector	549[2]
Endothall	0.1	Gas Chromatography-Liquid/Solid Extraction-Electron Capture Detector	548[2]
Endrin	0.002	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Ethylene dibromide (EDB)	0.00005	Gas Chromatography-Microextraction-Electron Capture Detector	504
Glyphosate	0.7	High Performance Liquid Chromatography-Post Column Reactor-Fluorescent Detector	547[2]
Heptachlor	0.0004	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Heptachlor epoxide	0.0002	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1
Hexachlorobenzene	0.001	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction-/Mass Spectroscopy	525.1
Hexachlorocyclopentadiene	0.05	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction-/Mass Spectroscopy	525.1
Lindane	0.0002	Gas Chromatography-Microextraction-Electron Capture Detector	505
		Gas Chromatography-Electron Capture Detector	508
		Capillary Column-Gas Chromatography-Liquid/Solid Extraction /Mass Spectroscopy	525.1

Table IV-2. Approved Methodology for Organic Contaminants

Contaminant	MCL mg/l	Methodology	Reference EPA[1]
p-Dichlorobenzene	0.075	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Gas Chromatography-Photoionization Detector	503.1
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
o-Dichlorobenzene	0.6	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Gas Chromatography-Photoionization Detector	503.1
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
1,2-Dichloroethane	0.005	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
1,1-Dichloroethylene	0.007	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
c-1,2-Dichloroethylene	0.07	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Capillary-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
t-1,2-Dichloroethylene	0.1	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
Dichloromethane(Methylene chloride)*	0.005	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
1,2-Dichloropropane	0.005	Purge and Trap; Gas Chromatography-Electrolytic Conductivity Detector	502.1
		Purge and Trap; Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap; Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap; Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
Ethylbenzene	0.7	Purge and Trap;Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap;Gas Chromatography-Photoionization Detector	503.1
		Purge and Trap;Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap;Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2
Styrene	0.1	Purge and Trap;Capillary Column-Gas Chromatography-Photoionization Detector-Electrolytic Conductivity Detector	502.2
		Purge and Trap;Gas Chromatography-Photoionization Detector	503.1
		Purge and Trap;Packed Column-Gas Chromatography/Mass Spectroscopy	524.1
		Purge and Trap;Capillary Column-Gas Chromatography/Mass Spectroscopy	524.2

V. SDWA (PLEASE COMPLETE AND RETURN WITH PRE-SURVEY PACKAGE)

MICROBIOLOGY LABORATORY ANALYSIS REVIEW CHECKLIST

LABORATORY West Virginia Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services

ADDRESS 167 11th Avenue

South Charleston, WV 25303

TELEPHONE NUMBER/FAX NUMBER (304) 558-3530 / (304) 558-2006

CONDUCTED BY _____

DATE _____

NAMES/TITLES/RESPONSIBILITIES OF KEY PERSONNEL INTERVIEWED

_____

_____

_____

_____

_____

V. SDWA (Please Complete and Return with PreSurvey Package)

Element	Yes	No	Comments
1. PERSONNEL			
1.1 Supervisor/Consultant			
Supervisor of analyst has a bachelor's degree in microbiology, biology, or equivalent with at least one college-level laboratory course in environmental microbiology, and has a minimum of two weeks course training or 80 hours of on-the-job training in water microbiology at a certified laboratory, or other training acceptable to the State or EPA	X		
If supervisor not available, consultant with same training and experience substituted, acceptable to the State, and present on-site frequently enough to satisfactorily perform a supervisor's duties	X		
1.2 Analyst (or equivalent job title)			
Analyst has a high school education, 3 months bench experience in microbiology, training in microbiological analysis of drinking water acceptable to the State (or EPA) and a minimum of 30 days on-the-job training under an experienced analyst	X		
Analyst demonstrated acceptable results for precision, specificity, and satisfactory analysis on unknown samples before analyzing compliance samples			
1.3 Waiver of Academic Training Requirement			
Need for specified academic training waived for highly experienced analysts	X		
1.4 Personnel Records			
Personnel records maintained on laboratory analysts include academic background, specialized training courses completed and types of microbiological analyses conducted	X		
2. LABORATORY FACILITIES			
Laboratory facilities clean, temperature and humidity controlled, with adequate lighting at bench top	X		
Sufficient space available for processing samples, bench top equipment, storage, cleaning glassware and sterilizing materials	X		
Provisions made for disposal of microbiological wastes	X		
3. LABORATORY EQUIPMENT AND SUPPLIES			
3.1 pH meter			
Accuracy and scale graduations within ± 0.1 units	X		
Buffer aliquot used only once	X		

Element	Yes	No	Comments
Electrodes maintained according to manufacturer's recommendations	X		
QC Meter standardized each use period with pH 7.0 and either 4.0 or 10.0 buffers, with date and buffers used recorded in log book 4/7/10 Three	X		3 pt calibration with slope
QC Commercial buffer solutions dated when received and opened and discarded before expiration date	X		
3.2. Balance (top loader or pan)			
Readability of 0.1 g	X		
QC Calibrated monthly using ASTM type 1, 2, or 3 weights (minimum 3 traceable weights which bracket laboratory weighing needs)	X		
QC Non-reference weights calibrated every six months with reference weights	X		
QC Annual service contract or internal maintenance protocol established, records available of most recent recalibration, and correction values on file and used	X		
QC Reference weight recertified if damaged or corroded	---		
3.3 Temperature Monitoring Device			
Temperature monitoring devices graduated in 0.5°C increments (0.2°C increments for tests which are incubated at 44.5°C) or less	X		
No separation in fluid column of glass thermometer	X		
No dial thermometers used which cannot be adjusted	---		
QC Glass and electronic thermometers calibrated annually, dial thermometers quarterly, at the temperature used against reference NIST thermometer or one meeting the requirements of NBS Monograph SP 250-23	X =		
QC Calibration factor marked on thermometer and calibration date and calibration factor recorded in QC record book	X		
QC Thermometer discarded if off more than 1°C from reference thermometer, reference thermometers recalibrated every 3-5 years	X		
QC Continuous recording devices used to monitor incubator temperature recalibrated annually as above	---		
3.4 Incubator Unit			
Incubator units have an internal temperature monitoring device and maintain temperature of 35 ± 0.5°C, and if used, 44.5 ± 0.2°C	X		

Element	Yes	No	Comments
Overcrowding avoided	X		
Oven thermometer graduated in 10°C increments or less, with bulb placed in sand during use	X		
QC Date, contents, sterilization time, temperature, and analyst's initials recorded for each cycle	X		
QC Spore strip or ampule used monthly	X		
3.7 Colony Counter			
Colony counter, dark field model, used to count Heterotrophic Plate Count colonies	X		
3.8 Conductivity Meter			
Suitable for checking laboratory reagent-grade water, readable in micromhos/cm or microsiemens/cm with measurement error not exceeding 1% or 1 micromhos/cm, whichever is more lenient	X		
QC Cell constant determined monthly	X		
In-line unit which cannot be calibrated not used to check reagent-grade water	X		
3.9 Refrigerator			
Maintains 1-5°C	X		
Thermometer graduated in 1°C increments or less, with thermometer bulb immersed in liquid	X		
QC Temperature recorded for days in use at least once per day	X		2 times per day
3.10 Inoculating Equipment			
Sterile metal or disposable plastic loops, wood applicator sticks, sterile swabs, or sterile plastic disposable pipet tips used	X		
Wood applicator sticks sterilized by dry heat	X		
Metal inoculating loops and needles made of nickel alloy or platinum (nickel alloy loops not used for oxidase test)	X		
3.11 Membrane Filtration (MF) Equipment			
MF units of stainless steel, glass, or autoclavable plastic, not scratched or corroded and do not leak	X		
QC Graduations on funnels used to measure sample volume checked for accuracy have tolerance of ≤2.5%, and a record of this calibration check retained	—		Used only on special projects. Only dilutions.
10x to 15x stereo microscope with fluorescent light source used to count sheen colonies	X		

Element		Yes	No	Comments
Required times for autoclaving material at 121°C (except for membrane filters and pads and carbohydrate-containing media, indicated times represent minimum times, dependent upon volumes, containers, and loads):				
- membrane filters and pads	10 min	---		
- carbohydrate containing media	12-15 min	X		
- contaminated test materials	30 min	X		
- membrane filter assemblies	15 min	X		45 min @132° C
- sample collection containers	15 min	X		
- individual glassware	15 min	X		
- dilution water blank	15 min	X		30 minutes
- rinse water (0.5 - 1 L)	15-30 min*	X		60 minutes
* time depends upon water volume per container and autoclave load				
Autoclaved membrane filters and pads and all media removed immediately after completion of sterilization cycle		---		
Membrane filter equipment autoclaved before beginning of first filtration series (filtration series ends when 30 minutes or longer elapses after a sample filtered)		X		
When UV light (254 nm) used to sanitize equipment, all supplies presterilized and QC checks conducted on UV lamp		---		
UV light used to control bacterial carry-over between samples during filtration series (optional)		---		
4.2 Sample Containers				
QC: Sterility of each lot of sample containers or bags confirmed by adding 25 mL of a sterile non-selective broth to at least one container, incubating at 35 ± 0.5°C for 24 hours and checking for growth		X		
4.3 Reagent-Grade Water				
Only satisfactorily tested reagent water from stills or deionization units used to prepare media, reagents and dilution/rinse water		X		

Element			Yes	No	Comments
QC Quality of reagent water should be tested and meets the following criteria:					
- conductivity	<2 micromhos/cm (microsiemens/cm) at 25°C	monthly	X		
- Pb, Cd, Cr Cu, Ni, Zn	not greater than 0.05 mg/L per contaminant, and no greater than 0.1 mg/L total	annually	X		
- total chlorine residual*	<0.1 mg/L	monthly	X		
- heterotrophic plate count*	<500/mL	monthly	X		
- bacteriological quality of reagent water*	ratio of growth rate 0.8:3.0	annually	—		No longer required.
*See section 4.3.2 of this chapter for additional details					
4.4 Dilution/Rinse Water					
Stock buffer solution or peptone water prepared as specified in Standard Methods			X		
Stock buffers autoclaved or filter-sterilized and containers labeled, dated, and refrigerated			X		
Stored stock buffer free of turbidity			X		
QC Each batch of dilution/rinse water checked for sterility by adding 50 mL of water to 50 mL double strength non-selective broth, incubating at 35 ± 0.5°C for 24 hours, and checking for growth			X		
4.5 Glassware Washing					
Distilled or deionized water used for final rinse			X		
QC Glassware inhibitory residue test performed on initial use of washing compound and whenever different formulation or washing procedure used			X		
QC Batches of dry glassware spot-checked for pH reaction			X		
Laboratory glassware washed with detergent designed for laboratory use			X		
5. ANALYTICAL METHODOLOGY					
5.1 General					

Element	Yes	No	Comments
QC Each new lot of dehydrated and prepared commercial medium checked before use with positive and negative culture controls and results recorded	X		
QC Each new batch of laboratory-prepared medium checked before use with positive and negative culture controls and results recorded	X		
Prepared plates refrigerated in sealed plastic bags or containers not longer than two weeks, with bag or container dated with preparation or expiration date	X		
Loose-cap tubes of broth stored at <30°C no longer than two weeks, tightly capped tubes no longer than 3 months at <30°C	X		
Refrigerated medium incubated at room temperature overnight before use and discarded if growth observed	X		
QC Parallel testing performed between a newly approved test procedure and another EPA-approved procedure for several months and/or several seasons (recommended)	X		
5.2 Membrane Filter (MF) Technique (for total coliforms in drinking water)	---		
Media			
M-Endo broth or agar or LES Endo agar in single step or enrichment technique used	---		
Ethanol not denatured	---		
Medium prepared in sterile flask and dissolved using boiling water bath or hot plate with stir bar	---		
Medium not boiled	---		
LES Endo agar medium pH 7.2 ± 0.2 M-Endo medium pH 7.2 ± 0.1	---		
MF broth refrigerated no longer than 96 hours, poured MF agar plates no longer than 2 weeks, ampuled M-Endo broth as per manufacturer's expiration date	---		
Uninoculated media discarded if growth or surface sheen observed	---		
QC Sterility check conducted on each funnel in use at beginning and end of each filtration series (filtration series ends when 30 minutes or more elapse between sample filtrations)	---		
QC If sterility control indicates contamination, all data rejected and another sample requested	---		

Element	Yes	No	Comments
Medium autoclaved at 121°C for 12-15 minutes			
Inverted vials in sterile medium free of bubbles and at least one-half to two-thirds covered after water sample added	X		
Refrigerated sterile MTF media incubated overnight at room temperature before use, with tubes/bottles showing growth and/or bubbles discarded	X		
Prepared broth media stored in dark at <30°C for no longer than 3 months in screw-cap tubes/bottles, two weeks for those with loose-fitting closures	---		
Media discarded if evaporation exceeds 10% of original volume	X		
Inoculated medium incubated at 35°C ± 0.5°C for 24 ± 2 hours	X		
If no gas or acid detected, inoculated medium incubated for another 24 hours	X		
All samples showing turbid culture (i.e., heavy growth, opaque) in the absence of gas/acid production invalidated and another sample collected from the same location (if laboratory performs confirmed test on turbid culture and confirmed test is total coliform-positive, sample reported as such, but if total coliform-negative, sample is invalidated)	X		
All 24- and 48-hour gas-positive or acid-positive tubes confirmed using BGLBB	X		
Completed Test not required	X		
When MTF test used on water supplies that have a history of confluent growth or TNTC by the MF procedure, all presumptive tubes with heavy growth without gas/acid production submitted to confirmed test and fecal coliform/*E. coli* test to check for coliform suppression	X		
5.4 Presence-Absence (P-A) Coliform Test (for drinking water)	---		
Medium	---		
When six-times formulation strength medium used, medium filter-sterilized, not autoclaved	---		
Medium autoclaved for 12 minutes at 121°C with total time in autoclave less than 30 minutes and with space between bottles	---		
Medium pH 6.8 ± 0.2	---		
Prepared medium stored in the dark at <30°C for no longer than 3 months	---		

Element	Yes	No	Comments
Medium pH 6.9 ± 0.1	---		
Inverted vials free of air bubbles and at least one-half to two-thirds covered after water sample added	---		
Loose-cap tubes stored in dark at room temperature no longer than 2 weeks, tightly closed screw-cap tubes no longer than 3 months when held in the dark at <30°C	---		
Water level in water bath above upper level of medium in culture tubes	X		
EC Medium incubated at 44.5°C ± 0.2°C for 24 ± 2 hours	X		
A-1 Medium incubated at 35°C ± 0.5°C for 3 hours, then at 44.5°C ± 0.2°C for 21 ± 2 hours	---		
Any gas detected in inverted vial considered fecal coliform positive	X		
5.6 Chromogenic/Fluorogenic Substrate Tests (MMO-MUG Test [Colilert] for total coliforms in source water and total coliforms and *E. coli* in drinking water; Colisure Test for total coliforms and *E. coli* in drinking water)			
Media			
Purchased from commercially available source only	X		
Media protected from light	X		
Colisure medium refrigerated until use, brought to room temperature before adding sample	---		
Each lot of medium checked for autofluoresence before use with 366-nm ultraviolet light with 6 watt bulb	X		
Medium which exhibits faint fluorescence discarded and another lot used	X		
Medium plus sample which exhibits color change before incubation discarded and another batch of medium used	X		
QC Each lot of medium checked by inoculating sterile water containing the medium with a MUG-positive *E. coli* strain, a MUG-negative coliform, and a non-coliform and analyzing them	X		
If Quanti-Tray or Quanti-Tray 2000 test used with Colilert medium, sealer checked monthly to determine leakage	X		
Glass bottles that contain inoculated medium checked with 366-nm ultraviolet light source with 6 watt bulb and discarded if fluorescence observed before incubation	---		

Element	Yes	No	Comments
MUG added to EC medium before autoclaving or commercially available EC + MUG used	---		
Final MUG concentration 50 μg/mL	---		
Medium pH 6.9 ± 0.2	---		
Inverted vial omitted (optional)	---		
Test tubes and autoclaved medium checked for autofluorescence before use with 366-nm UV light	---		
If fluorescence exhibited, non-fluorescing tubes or another lot of medium that does not fluoresce used or MUG-positive (*E. coli*) and a MUG-negative (e.g. uninoculated) control included for each analysis	---		
Prepared medium in tubes with loose-fitting closures used within two weeks, or three months for tightly closed screw-cap tubes when held in the dark at <30°C	---		
Uninoculated medium with growth discarded	---		
QC Each lot of commercially prepared medium and each batch of laboratory-prepared medium checked by inoculating LTB with positive and negative culture controls, incubating at 35°C ± 0.5°C for 24 hours and then transferring to EC Medium + MUG for further incubation at 44.5°C ± 0.2°C for 24 hours, with results read and recorded	---		
Water level of water bath above upper level of medium	---		
Incubated at 44.5° ± 0.2°C for 24 ± 2 hours	---		
Fluorescence checked using UV lamp (366-nm) with 6 watt bulb in a darkened room	---		
5.8 Nutrient Agar + MUG Test (for *E. coli*)	--		
Medium	---		
Medium autoclaved in 100 mL volumes at 121°C for 15 minutes	---		
MUG added to Nutrient Agar before autoclaving or Nutrient Agar + MUG purchased commercially	---		
Final MUG concentration 100 μg/L	---		
Medium pH 6.8 ± 0.2	---		
Medium in petri dishes stored refrigerated in plastic bag or tightly closed container and used within two weeks	---		
Refrigerated sterilized medium incubated at room temperature overnight and plates with growth discarded	---		

Element	Yes	No	Comments
Countable plates obtained for most potable waters by plating 1.0 mL and/or 0.1 mL volume of undiluted sample	X		
At least duplicate plates per dilution used	X		
(For Pour Plate Method)			
Sample pipetted aseptically into bottom of petri dish and then 12-15 mL tempered melted agar added	X		
Sample mixed with spillage avoided	X		
After solidification on level surface, plates inverted and incubated at 35°C ± 0.5°C for 48 ± 3 hours	X		
Plates stacked no more than four high	X		
(For Spread Plate Method)			
0.1 or 0.5 mL of sample or dilution pipetted onto surface of pre-dried agar plate and inoculum spread over entire agar surface using sterile bent glass rod	N/A		
Inoculum absorbed completely before plates inverted and incubated at 20-28°C for 5-7 days	N/A		
(For Membrane Filter Technique)	N/A		
Volume filtered to yield between 20-200 colonies	N/A		
Filter transferred to petri dish containing 5 mL solidified R2A medium and incubated at 20-28°C for 5-7 days	N/A		
Petri dishes with loose-fitting lids placed in container with close fitting lid and moistened paper towels	N/A		
Colonies counted using stereoscopic microscope at 10-15X magnification	N/A		
(For Pour Plate and Spread Plate Techniques)	X		
Colonies counted manually using dark field colony counter	X		
Only plates with 30 to 300 colonies counted, except for plates inoculated with 1.0 mL of undiluted sample	X		
Fully automatic colony counters not used	X		
QC Medium sterility verified by pouring final control plate and data rejected if control contaminated	X		
5.10 Membrane Filter Technique (for enumerating total coliforms in source water)	X		
Same as Section 5.2, Membrane Filter Technique (for total coliforms in drinking water), except invalidation does not apply	X		

Element	Yes	No	Comments
QC If two or more analysts available, each counts fecal coliform colonies on same membrane monthly and counts agree within 10%	X		
5. SAMPLE COLLECTION, HANDLING, AND PRESERVATION			
6.1 Sample Collector			
Trained in aseptic sampling procedures and, if required, approved by appropriate regulatory authority or designated representative	X		
6.2 Sampling			
Sample representative of water distribution system	X		
Water taps used for sampling free of aerators, strainers, hose attachments, mixing type faucets, and purification devices	X		
Cold water tap used	X		
Service line cleared before sampling by maintaining steady water flow for at least 2 minutes	X		
At least 100 mL sample volume collected, allowing one inch air space in container	X		
Sample information form completed immediately after sample collection	X		
Source water representative of supply, collected not too far intake at a reasonable distance from shore	X		
6.3 Sample Icing			
Samples held at < 10°C during transit to laboratory (recommended for drinking water, required for source water)	N/A		
6.4 Sample Holding/Travel Time			
Time from sample collection to initiation of analysis for total coliforms, fecal coliforms, or *E. coli* does not exceed 30 hours for drinking water samples	X		
Time from sample collection to initiation of analysis for total coliforms and fecal coliforms in source water and heterotrophic bacteria in drinking water does not exceed 8 hours	N/A		
All samples analyzed on day of receipt by laboratory, unless laboratory receives sample late in day and then refrigerates sample overnight and begins analysis within holding time	X		
6.5 Sample Information Form			

Element	Yes	No	Comments
Sampling records include: - sample information form, from Section 6.5 - date and time of sample receipt by laboratory - name of laboratory person receiving sample - if any deficiency in sample condition noted, sample, at a minimum, flagged - if sample transit time exceeds 30 hours (8 hours for source water samples), sample tagged	X		
8.4 Analytical Records			
Data recorded in ink with changes lined through such that original entry visible and with changes initialed and dated	X		
Analytical records include: - laboratory sample identification - date and time analysis begins - laboratory and person(s) responsible for performing analysis - analytical technique or method used - all items marked QC - results of analysis	X		
8.5 Preventive Maintenance			
Preventive maintenance and repair records for all instruments and equipment kept for 5 years	X		
9. ACTION RESPONSE TO LABORATORY RESULTS			
9.1 Testing Total Coliform-Positive Cultures			
For the Total Coliform Rule, all total coliform positive cultures tested for presence of either fecal coliforms or *E. coli*	X		
9.2 Notification of Positive Results			
For Total Coliform Rule, proper authority notified promptly by laboratory of positive total coliform, fecal coliform or *E. coli* results	X		
Total coliform positive result based on confirmed phase for MTF Technique and P-A Coliform Test or verified test for MF Technique (no requirement for confirmation of positive Colilert/Colisure, fecal coliform or *E. coli* tests)	X		
9.3 Invalidation of Total Coliform-Negative Sample			
For Total Coliform Rule, proper authority notified when results indicate non-coliforms may have interfered with total coliform analysis	X		

990342	8-31-99	9-1-99	9-1-99	✓	9-8-99	ZO
990342DDP				✓		
990343				✓		
990343LFSM				✓		
Digestion Tube Checked for 35 ml Volume? Yes/OK						
990343	8-31-99	9-1-99	9-1-99	✓	9-8-99	ZO
990354	8-30-99	9-2-99	9-2-99	✓		
990354DDP				✓		
990355	8-31-99			✓		
990355LFSM				✓		
Digestion Tube Checked for 35 ml Volume? Yes/OK						
990358	9-3-99	9-14-99	9-14-99	✓	9-15-99	ZO
990358DDP				✓		
990358LFSM				✓		
990359	9-13-99			✓		
990359DDP				✓		
990359LFSM				✓		
Digestion Tube Checked for 35 ml Volume? Yes/OK						
990362	9-15-99	9-16-99	9-16-99	✓	9-17-99	ZO
990362DDP				✓		
990362LFSM				✓		
Digestion Tube Checked for 35 ml Volume? Yes/OK						
990363	9-18-99	9-20-99	9-20-99	✓	9-22-99	ZO
990363DDP				✓		
990363LFSM				✓		
990364	9-17-99	9-20-99	9-20-99	✓	9-22-99	ZO
990364DDP				✓		
990365				✓		
990365LFSM				✓		
Digestion Tube Checked for 35 ml Volume? Yes/OK						
990362	9-15-99	9-16-99	9-16-99	✓	9-27-99	ZO
990362DDP				✓		
990362LFSM				✓		

5.2%
1% + 2% H_2O_2
2 + 2%

990362 Turb. = 0.12
Evap. at 1% + HNO_3
for 1 l
"DA"

Performance Evaluation Report
USEPA Water Supply Study WS038

Participant ID: WV00003 Type: STATE Requesting Office: R03

	Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
TRACE METALS IN MICROGRAMS PER LITER:					
001-ARSENIC					
	001	84.5	83.1	71.7- 88.4	Accept.
002-BARIUM					
	002	2280	2002	1700- 2300	Accept.
003-CADMIUM					
	001	2.15	2.12	1.7- 2.54	Accept.
004-CHROMIUM					
	001	146	148	126- 170	Accept.
005-LEAD					
	001	54.4	56.2	39.3- 73.1	Accept.
006-MERCURY					
	001	5.25	6.39	4.47- 8.31	Accept.
007-SELENIUM					
	001	96.4	89.3	71.4- 107	Accept.
091-COPPER					
	001	1230	1203	1080- 1320	Accept.
140-ANTIMONY					
	002	6.41	6.48	4.54- 8.42	Accept.
141-BERYLLIUM					
	001	10.4	10.1	8.59- 11.6	Accept.
142-NICKEL					
	001	240	240	204- 276	Accept.
236-MANGANESE					
	001	414	411	372- 420	Accept.
237-MOLYBDENUM					
	002	18.4	16.2	13- 19.5	Accept.
239-ZINC					
	001	2760	2914	2620- 3080	Accept.
NITRATE/NITRITE/FLUORIDE IN MILLIGRAMS PER LITER:					
009-NITRATE AS N					
	001	4.17	4.10	3.69- 4.51	Accept.
092-NITRITE AS N					
	001	1.64	1.60	1.36- 1.84	Accept.
INSECTICIDES IN MICROGRAMS PER LITER:					
011-ENDRIN					
	001	0.212	0.467	0.327-0.607	Not Accept.
012-LINDANE					
	001	0.510	0.621	0.342- 0.9	Accept.
013-METHOXYCHLOR					
	001	38.6	34.8	19.1- 50.5	Accept.
014-TOXAPHENE					
	002	7.86	12.7	6.99- 18.4	Accept.

Performance Evaluation Report
USEPA Water Supply Study WS038

Participant ID: WV00003 Type: STATE Requesting Office: FO3

Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
093-ALACHLOR				
005	2.47	9.52	5.24- 13.8	Not Accept.
094-ATRAZINE				
005	7.76	12.8	7.04- 18.6	Accept.
095-HEPTACHLOR				
004	1.18	1.20	0.66- 1.74	Accept.
096-HEPTACHLOR EPOXIDE				
004	0.614	0.742	0.408- 1.08	Accept.
097-CHLORDANE (TOTAL)				
003	10.1	8.20	4.51- 11.9	Accept.
112-HEXACHLOROCYCLOPENTADIEN				
004	1.09	1.47	0.0583- 2.01	Accept.
113-SIMAZINE				
005	7.72	8.77	1.87- 14.2	Accept.
172-HEXACHLOROBENZENE				
004	0.204	0.538	0.213-0.683	Not Accept.
241-METOLACHLOR				
006	19.6	24.8	11.2- 36.6	Accept.
242-METRIBUZIN				
006	2.22	16.9	D.I. - 26	Accept.
244-TRIFLURALIN				
004	1.33	1.76	0.691- 2.31	Accept.
256-ALDRIN				
004	0.382	0.358	0.164- 0.45	Accept.
258-DIELDRIN				
004	0.57	0.683	0.466-0.896	Accept.
259-PEDEACHLOR				
004	1.39	1.46	0.823- 2.19	Accept.
VOLATILE ORGANIC COMPOUNDS IN MICROGRAMS PER LITER:				
045-1,2DIBROMO3CHLOROPROPANE				
004	0.35	0.429	0.257-0.601	Accept.
046-ETHYLENE DIBROMIDE (EDB)				
004	0.32	0.336	0.202- 0.47	Accept.
MISCELLANEOUS ANALYTES:				
022-RESIDUAL FREE CHLORINE(MILLIGRAMS PER LITER)				
001	0.680	0.820	0.662-0.963	Accept.
023-TURBIDITY(NTU'S)				
001	6.30	5.89	4.72- 6.77	Accept.
024-TOTAL FILTERABLE RESIDUE(MILLIGRAMS PER LITER)				
001	331	419	249- 622	Accept.
025-CALCIUM HARDNESS(MG. CACO3/L)				
001	225	240	221- 252	Accept.
026-PH-UNITS				
001	9.14	9.13	8.89- 9.31	Accept.

Performance Evaluation Report
USEPA Water Supply Study WS038

Participant ID: WV0000003 Type: STATE Requesting Office: FC3

Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
027-ALKALINITY(MG. CACO3/L)				
001	47.5	43.5	42.4- 49.9	Accept.
029-SODIUM(MILLIGRAMS PER LITER)				
001	21.7	20.0	19.1- 22.2	Accept.

********** END OF DATA FOR WV00003 **********
NOTE: FOR LIMITS AND TRUE VALUES, ASSUME THREE SIGNIFICANT DIGITS.
********** END OF REPORT FOR WV0000003 **********

* Based on gravimetric calculations, or a reference value when necessary.

Report: PE005
Page: 1
Date: 25SEP97

Performance Evaluation Report
USEPA Water Supply Study WS039

Participant ID: WV00003 Type: STATE Requesting Office: R03

Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
TRACE METALS IN MICROGRAMS PER LITER:				
002-BARIUM				
001	1110	1100	935- 1270	Accept.
226-BORON				
002	643	599	573- 670	Accept.
NITRATE/NITRITE/FLUORIDE IN MILLIGRAMS PER LITER:				
010-FLUORIDE				
001	2.84	2.90	2.61- 3.19	Accept.
MISCELLANEOUS ANALYTES:				
145-SULFATE(MILLIGRAMS PER LITER)				
001	434.0	490	440- 538	Not Accept.

********** END OF DATA FOR WV00003 **********
NOTE: FOR LIMITS AND TRUE VALUES, ASSUME THREE SIGNIFICANT DIGITS.
********** END OF REPORT FOR WV00003 **********

* Based on gravimetric calculations, or a reference value when necessary.

Performance Evaluation Report
USEPA Water Supply Study WS040

Participant ID: WV00003 Type: STATE Requesting Office: RC3

	Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
TRACE METALS IN MICROGRAMS PER LITER:					
001-ARSENIC	001	112	102	89.3- 113	Accept.
002-BARIUM	001	3020	2700	2300- 3110	Accept.
003-CADMIUM	001	5.99	6.31	5.05- 7.57	Accept.
004-CHROMIUM	001	95.7	90.9	77.3- 105	Accept.
005-LEAD	001	68.6	71.0	49.7- 92.3	Accept.
006-MERCURY	001	1.40	1.50	1.05- 1.95	Accept.
007-SELENIUM	001	79.5	74.0	59.2- 88.8	Accept.
091-COPPER	001	1680	1700	1530- 1870	Accept.
140-ANTIMONY	001	14.0	13.0	9.1- 16.9	Accept.
141-BERYLLIUM	001	6.58	6.60	5.61- 7.59	Accept.
142-NICKEL	001	25.9	25.0	21.3- 28.8	Accept.
226-BORON	002	1230	1150	1050- 1290	Accept.
236-MANGANESE	002	30.0	32.0	27.7- 35.2	Accept.
237-MOLYBDENUM	002	38.2	35.0	29.6- 40.1	Accept.
239-ZINC	002	1750	1700	1620- 1850	Accept.
NITRATE/NITRITE/FLUORIDE IN MILLIGRAMS PER LITER:					
009-NITRATE AS N	001	7.19	7.10	6.39- 7.81	Accept.
010-FLUORIDE	001	1.31	1.29	1.16- 1.42	Accept.
092-NITRITE AS N	001	1.7	1.30	1.11- 1.5	Not Accept.
261-ORTHOPHOSPHATE AS P	001	2.65	0.820	0.745-0.882	Not Accept.
MISCELLANEOUS ANALYTES:					
022-RESIDUAL FREE CHLORINE (MILLIGRAMS PER LITER)	001	0.35	0.240	0.0199-0.368	Accept.
023-TURBIDITY (NTU'S)	001	7.81	7.80	7- 9.67	Accept.

Performance Evaluation Report
USEPA Water Supply Study WS040

Participant ID: WV0000003 Type: STATE Requesting Office: F03

Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
024-TOTAL FILTERABLE RESIDUE(MILLIGRAMS PER LITER)				
001	204	232	147- 380	Accept.
025-CALCIUM HARDNESS(MG. CACO3/L)				
001	92.0	95.0	88- 104	Accept.
026-PH-UNITS				
001	9.17	9.13	8.93- 9.33	Accept.
027-ALKALINITY(MG. CACO3/L)				
001	36.0	34.4	32.8- 39.6	Accept.
029-SODIUM(MILLIGRAMS PER LITER)				
001	15.9	15.8	14.4- 17.8	Accept.
145-SULFATE(MILLIGRAMS PER LITER)				
001	198.9	225	202- 247	Not Accept.

********** END OF DATA FOR WV0000003 **********
NOTE: FOR LIMITS AND TRUE VALUES, ASSUME THREE SIGNIFICANT DIGITS.
********** END OF REPORT FOR WV0000003 **********

* Based on gravimetric calculations, or a reference value when necessary.

Performance Evaluation Report
USEPA Water Supply Study WS041

Participant ID: WV00003 Type: STATE Requesting Office: R03

Sample Number	Reported Value	True Value*	Acceptance Limits	Performance Evaluation
TRACE METALS IN MICROGRAMS PER LITER:				
143-THALLIUM				
001	3.34	3.50	2.45- 4.55	Accept.
NITRATE/NITRITE/FLUORIDE IN MILLIGRAMS PER LITER:				
092-NITRITE AS N				
001	1.66	1.70	1.45- 1.96	Accept.
261-ORTHOPHOSPHATE AS P				
001	1.98	1.30	1.19- 1.39	Not Accept.
MISCELLANEOUS ANALYTES:				
145-SULFATE(MILLIGRAMS PER LITER)				
001	46.84	49.0	44.1- 54.2	Accept.

********** END OF DATA FOR WV00003 **********
NOTE: FOR LIMITS AND TRUE VALUES, ASSUME THREE SIGNIFICANT DIGITS.
********** END OF REPORT FOR WV00003 **********

* Based on gravimetric calculations, or a reference value when necessary.

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-37 Inorganic Final Report

ERA Laboratory Code: W2134-01 EPA ID: WV00003 State ID: 00003C Report Issued: 10/22/99

ERA Standard	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Metals	Aluminum	µg/l	85.6	81.9	70.3 - 95.0	Acceptable	3113B
	Antimony	µg/l	33.5	36.0	25.2 - 46.8	Acceptable	3113B
	Arsenic	µg/l	116	109	95.4 - 122	Acceptable	3113B
	Barium	µg/l	2210	2170	1840 - 2500	Acceptable	200.7
	Beryllium	µg/l	5.60	5.63	4.79 - 6.47	Acceptable	3113B
	Boron	µg/l		766	715 - 843		
	Cadmium	µg/l	26.1	26.1	20.9 - 31.3	Acceptable	3113B
	Calcium (mg/l)	mg/l		55.0	47.9 - 64.0		
	Chromium	µg/l	95.4	95.8	81.4 - 110	Acceptable	3113B
	Copper	µg/l	77.8	79.0	71.1 - 86.9	Acceptable	3113B
	Iron	µg/l	117	99.3	77.3 - 121	Acceptable	3113B
	Lead	µg/l	60.2	60.0	42.0 - 78.0	Acceptable	3113B
	Manganese	µg/l	312	351	326 - 369	Not Acceptable	3111B
	Molybdenum	µg/l		22.0	18.1 - 25.9		
	Nickel	µg/l	176	179	152 - 206	Acceptable	3113B
	Selenium	µg/l	42.6	38.4	30.7 - 46.1	Acceptable	3113B
	Silver	µg/l		65.9	56.7 - 74.5		
	Thallium	µg/l	4.99	4.62	3.23 - 6.01	Acceptable	200.9
	Zinc	µg/l	568	572	524 - 616	Acceptable	3111B
	Hardness as CaCO3	mg/l		137	128 - 148		
Mercury	Mercury	µg/l	2.00	2.60	1.82 - 3.38	Acceptable	245.1
Titration Hardness	Hardness as CaCO3	mg/l	146	146	137 - 157	Acceptable	3500D

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-37 Inorganic Final Report

ERA Laboratory Code: W2134-01 EPA ID: WV00003 State ID: 00003C Report Issued: 10/22/99

ERA Standard	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
pH	pH	S.U.		6.20	5.58 - 6.82		
Inorganics	Bromide	mg/l		0.395	0.339 - 0.457		
	Chloride	mg/l	8.12	8.20	7.29 - 9.25	Acceptable	300.0
	Conductivity (µmhos)	µmhos	365	383	320 - 436	Acceptable	2510B
	Fluoride	mg/l	4.54	5.65	5.09 - 6.22	Not Acceptable	300.0
	Nitrate as N	mg/l	6.30	6.45	5.81 - 7.10	Acceptable	353.2
	Potassium	mg/l		29.8	25.6 - 34.8		
	Sulfate	mg/l	45.8	45.1	40.3 - 49.7	Acceptable	300.0
	Total dissolved solids	mg/l	330	336	218 - 454	Acceptable	160.1
Alkalinity & Sodium	Alkalinity (as CaCO3)	mg/l		47.1	44.7 - 52.8		
	Sodium	mg/l		21.7	20.1 - 23.9		
Turbidity	Turbidity	NTU	3.96	4.33	3.79 - 5.18	Acceptable	180.1
Residual Chlorine	Free residual chlorine	mg/l		3.96	3.39 - 4.53		
	Total residual chlorine	mg/l		4.21	3.15 - 4.94		
Nitrite	Nitrite as N	mg/l	1.69	1.55	1.32 - 1.78	Acceptable	353.2
Nutrients	ortho-Phosphate as P	mg/l		0.590	0.520 - 0.639		
Cyanide	Cyanide	mg/l		0.472	0.354 - 0.590		
TOC	Total organic carbon	mg/l		4.03	3.63 - 4.63		
Chlorite	Chlorite	µg/l		549	394 - 816		
Bromate & Chlorate	Bromate	µg/l		44.9	21.4 - 65.6		
	Chlorate	µg/l		125	102 - 144		

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-37 Score and Overall Assessment

ERA Laboratory Code: W2134-01 EPA ID: WV00003 State ID: 00003C Report Issued: 10/22/99

Number of Acceptable Analytes	Number of Reported Analytes	InterLaB™ Score	Overall Assessment
23	25	92.0%	Very Good

Scoring Definitions:

- The **Number of Acceptable Analytes** is equal to any reported values that resulted in an "Acceptable" performance evaluation for the laboratory. An acceptable performance evaluation falls with in the Acceptance Limits.

- The **Number of Reported Analytes** is equal to any evaluated values reported during this study.

- The **InterLaB™ Score** is equal to the sum of the Number of Acceptable Analytes divided by the total Number of Reported Analytes.

- The **Overall Assessment:**
  Excellent = InterLaB™ Score falls within 95.0% and 100%.
  Very Good = InterLaB™ Score falls within 85.0% and 94.9%.
  Good = InterLaB™ Score falls within 75.0% and 84.9%.
  Acceptalbe = InterLaB™ Score falls within 65.0% and 74.9%.
  Needs Improvement = InterLaB™ Score ins equal to or below 64.9%.

ENVIRONMENTAL
RESOURCE ASSOCIATES

September 29, 1999

Charles Jones
Environmental Assessment & Protection Division
U.S. EPA, Region 3
840 Chestnut Building (3ESOO)
Philadelphia, PA 19107

Dear Charles:

On August 5, 1999, WV Bureau of Public Health located in Charleston, West Virginia, participated in ERA's QuiK™ Response Performance Evaluation Program. The following results were reported to ERA by WV Bureau of Public Health for the PE standard, lot 08059907. The Certified Values and the QuiK™ Response Acceptance Limits were not available to WV Bureau of Public Health.

If you have any questions, please contact Shawn Kassner, InterLaB™ Administrator, or me at 1-800-372-0122.

Sincerely,

Roland P. Bruggeman
InterLaB™ Chemist

rpb
attachments

5540 MARSHALL STREET, ARVADA, COLORADO 80002
TEL (303) 431-8454 FAX (303) 421-0159 www.eraqc.com

ENVIRONMENTAL RESOURCE ASSOCIATES®

QuiK™ Response PE Standards

Final Report

Corrosivity

Customer: WV Bureau of Public Health
Lot Number: 08059907
State ID Number: WV00003

Parameter	Units	Reported Value	Certified Value	QuiK™ Response Limits	Comment
pH	S.U.	9.06	9.23	9.03 - 9.43	Within Limits
Alkalinity	mg/L	343	331	295 - 367	Within Limits
TDS	mg/L	1001	1010	879 - 1140	Within Limits
Calcium	mg/L	134	54.3	46.7 - 61.9	Outside Limits
Sodium	mg/L	159	152	129 - 175	Within Limits
Saturation Index	S.I.		1.90	1.16 - 2.56	

Results reported by: Wayne Morganroth - WV Bureau of Public Health

Date of Report: 9/29/99

This parameter was mistakenly reported out as Calcium Hardness (as $CaCO_3$) since this is the normal way it is reported out to and for program people - District Engineers - this is then used by them to calculate a Langelier corrosivity index. If the value of 134 mg/L of calcium carbonate is converted to calcium the value obtained is:

Calcium = 134 mg/L $CaCO_3$ x ($Ca/CaCO_3$) gravimetric factor

Calcium = 134 x).40044 * = 53.6 mg/L

* Gravimetric factor value obtained from the 14th Edition of Lange's Handbook of Chemistry.

Wayne

Freedom_0006095_0106

ENVIRONMENTAL
RESOURCE ASSOCIATES®

October 22, 1999

Wayne Morganroth
Bureau of Public Health, Ols
Environmental Chemistry Lab
4710 Chimney Dr Ste G
Charleston, WV 25302

Dear Wayne Morganroth :

Enclosed is ERA's final statistical summary for the InterLaB WatR™ Supply WS-37 Proficiency Testing (PT) Program. ERA's format for the InterLaB WatR™ Supply statistical summary is based on the USEPA's National Standards for Water Proficiency Testing Studies Criteria Document, December 1998. Our records also indicate that you have requested reports be sent to the State of West Virginia. At this time, this state has not provided guidlines to PT providers regarding issuance of reports. When notified by this state that it will accept PT reports, ERA will automatically forward a copy of your report. This concludes the WS-37 study.

Thank you for your participation in the InterLaB WatR™ Supply WS-37 Performance Evaluation Program. If you have any questions, please do not hesitate to call Roland P. Bruggeman, InterLaB™ Chemist, or me at 1-800-372-0122.

Sincerely,

Shawn Kassner
InterLaB™ Administrator

attachments
smk

5540 MARSHALL STREET, ARVADA, COLORADO 80002
TEL (303) 431-8454 FAX (303) 421-0159 www.eraqc.com

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-37 Definitions & Study Discussion

ERA Laboratory Code: W2134-01 EPA ID: WV00003 State ID: 00003C Report Issued: 10/22/99

InterLaB WatR™ SupplyDefinitions:

The **Reported Value** is the value that the laboratory reported to ERA.

The **ERA Assigned Value** is equal to 100% of the parameter present in the standard as determined by gravimetric and/or volumetric measurements made during standard preparation as applicable. A parameter not added to the standard is given an **Assigned Value** of **"Zero"** per the guidelines contained in the EPA's National Standards for Water Proficiency Testing Criteria Document, December 1998 as applicable.

The **Acceptance Limits** are established per the guidelines contained in the EPA's National Standards for Water Proficiency Testing Criteria Document, December 1998 as applicable.

The **Performance Evaluation:**

Acceptable = Reported Value falls within the Acceptance Limits.

Not Acceptable = Reported Value falls outside the Acceptance Limits.

No Evaluation = Reported Values that can not be evaluated.

The **Method Description** is the method the laboratory reported to ERA.

D.L. equals the Detection Limit.

InterLaB WatR™ Supply Study Discussion:

ERA WatR™ Supply Proficiency Testing Study 37 has been reviewed by ERA Senior Management and certified compliant with the requirements of the USEPA's National Standards for Water Proficiency Testing Studies Criteria Document, December 1998, and those contained in the National Institute for Standards and Technologies Handbooks 150 and 150-19.

Per the requirements of the USEPA's Criteria Document and the NIST NVLAP Handbooks, the WatR™ Supply 37 (WS 37) results were examined for any study anomalies. A full review of all homogeneity, stability, and accuracy verification data was completed. All analytical verification data for all analytes in the WS 37 standards met the acceptance criteria contained in the US EPA's National Criteria Document for Water Proficiency Testing Studies, December 1998, and the National Voluntary Laboratory Accreditation Program, Handbook 150-19 for Chemical Calibration for Providers of Proficiency Testing, June 1999.

The data submitted by participating laboratories was also examined for study anomalies. Based upon ERA's review of the data, all Acceptance Limits for the InterLaB WatR™ Supply study, WS37, were calculated based on the US EPA's National Criteria Document for Water Proficiency Testing Studies, December 1998, as applicable, except for dichlorodifluoromethane, bromoacetic acid, and chloroacetic acid. The data submitted by participating laboratories for these three components indicated a method specific bimodal distribution of data. After reviewing the data, the following changes were made to the upper Acceptance limits for these analytes.

- The dichlorodifluoromethane upper Acceptance Limit was changed from 20.4 µg/L to 28.2 µg/L.
- The bromoacetic acid upper Acceptance Limit was changed from 17.2 µg/L to 22.7 µg/L.
- The chloroacetic acid upper Acceptance Limit was changed from 14.2 µg/L to 20.7 µg/L.

The changes were approved by ERA Senior Management, and made according to the guidance provided in the USEPA's National Criteria Document page 1-2. If you have any questions regarding WatR™ Supply Study WS 37, please contact Shawn Kassner, InterLaB™ Program Coordinator, or Roland P. Bruggeman, InterLaB™ Chemist, at 1-800-372-0122.

Final Microbiology
SDWA Laboratory Evaluation Report
Rev. 2-21-00

Office of Laboratory Services
Department of Health and Human Resources
Bureau for Public Health
State of West Virginia

167 11th Avenue
South Charleston, WV 25303

On-site Evaluation Performed

on

Nov. 29 - Dec. 1, 1999

by

David E. Russell
Microbiological Evaluator

Office of Analytical Services and Quality Assurance
Environmental Science Center
U.S. Environmental Protection Agency, Region III
Ft. Meade, MD 20755-5350

I. Introduction

The microbiology laboratory is currently analyzing drinking and source water for total coliforms using Colilert (MMO-MUG), the Multiple-Tube Fermentation (MTF) technique (100 ml sample volume and bromocresol purple acid indicator), the Membrane Filtration (MF) technique, or Quanti-Tray, each followed by the appropriate procedures for fecal coliforms (or *E. coli*). Heterotrophic Plate Count (HPC) determinations are also performed on lab reagent water using the pour plate method.

Since the last EPA inspection in September of 1996, performance evaluation (PE) samples for total and fecal coliforms (or *E. coli*) have been successfully analyzed using Colilert, MTF, and MF methods in 1997 and 1998. The laboratory analytical staff should be commended for the analytical proficiency demonstrated by this record of PE analyses. PE samples were not analyzed in 1999.

The equipment and procedures employed in the bacteriological analyses of drinking water by this laboratory conform with the provisions of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA) , except as described in section III below.

II. Personnel

The following personnel currently analyze drinking and source water for total and fecal coliforms (or *E. coli*) using the Colilert, MTF (100ml volume), MF, or Quanti-Tray methods, and perform HPC analyses on lab reagent water:

Tom Ong
Joyce Vance-Abshire
Mike Flesher
Tracey Bossie
Joe Cochran
Micah Moore

The last three individuals listed have been at the state laboratory less than one year.

The inspector wishes to thank the Microbiology Supervisor, Microbiologists, and Lab Assistants for their cooperation and assistance during the on-site evaluation.

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III. Deviations

Deviations from the equipment and analytical procedures in the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA) are as listed below. Note that all chapter, page, or paragraph numbers and quotes are from the manual.

A. As stated in Chapter III (p.III-4), a laboratory analyzing drinking water should prepare a *written* description of its QA/QC activities (a QA plan), the purpose of which is to "ensure that routinely generated analytical data are scientifically valid and defensible, and are of known and acceptable precision and accuracy." QC procedures are to be specified in SOPs *written* for each method used. Furthermore, it is "the responsibility of the QA manager to keep the QA plan up to date". Although SOPs have been drafted for the Colilert and HPC methods, no SOPs exist for the MTF method (used daily to analyze drinking water) or the occasionally used MF and Quanti-Tray techniques. Nor are there written QA/QC procedures for the use and maintenance of laboratory equipment or general laboratory procedures common to all methods. Therefore, although a few of the elements exist in draft form, there is no complete comprehensive QA plan for drinking water microbiology.

B. Chapter III requires that laboratories, in order to maintain SDWA certification status, analyze PE samples annually. The purpose of this requirement is to confirm that the analytical proficiency of the laboratory is maintained over time despite changes in equipment and personnel that may occur. Although PE samples were successfully analyzed by the Laboratory in 1997 and 1998, none was analyzed in 1999. According to the manual (p. III-7), this omission alone is sufficient basis for downgrading certification status to "provisionally certified".

C. Paragraph 1.2(Chapter V) states that "before analyzing compliance samples, the analyst must demonstrate acceptable results for precision, specificity, and satisfactory analysis on unknown samples." Currently the Laboratory has no record of such a demonstration of analytical proficiency for each new analyst, although other records assessing analyst knowledge are being kept. Note that the above mentioned "unknown samples" could be prepared by the supervisor.

D. The Laboratory should be highly commended for it's practice of rejecting (without analysis) all *drinking water* samples that exceed the 30 hour holding time. *Source water*, however, has a sample holding time of 8 hours (paragraph 6.4 and Surface Water Treatment Rule, 40 CFR 141.74(a)), the purpose of which is to minimize changes in the sample's bacterial assemblage during the period between collection and analysis. Currently this holding time is regularly exceeded because *source water* samples are routinely analyzed the morning after the day they are collected. In addition negative results for the samples that have exceeded the holding time are not flagged as required by paragraph 8.3.5 (as modified in "Errata").

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IV. Recommendations

The following remarks are offered as suggestions to help improve the quality and integrity of the data the laboratory generates. Note that all paragraph numbers and quotes are from Chapter V of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA).

A. According to paragraph 3.1.5, all pH buffers used "should be dated upon receipt and when opened." Of the three buffer solutions (4.0, 7.0, 10.0) currently in use, two had only the date received marked on them and the third no dates at all. It is recommended as a matter of good laboratory practice that dates received and opened, and the initials of the analyst recording those dates, be marked on all pH buffers in use.

B. According to paragraphs 3.3.2, calibrations of glass and electronic thermometers should be checked annually against an NIST reference thermometer and the results recorded in a log book. Although considerable records of thermometer calibrations were available, they were not organized in such a way as to easily determine the history of calibration of individual thermometers. This problem had been already identified by the Laboratory and a new form or log sheet had been create, but was not yet in use at the time of the on-site visit. One of the new forms will be used for each thermometer; therefore, the record of calibrations for any one thermometer will be readily available. The Laboratory should be commended for this improvement in record keeping.

C. A further improvement in temperature record keeping would be to re-design the temperature recording tables to include the thermometer reading and the corrected temperature for each time the thermometer is read. When only the corrected temperature is recorded, there is no documentation that the analyst actually corrected the thermometer reading with the appropriate correction factor.

D. Regarding records kept for each autoclave, it is recommended that the autoclave for which the records are being kept be clearly indicated on the record form. Although the clip board with the autoclave records hangs next to the relevant autoclave, there is no association recorded on paper between the records and the autoclave.

E. According to paragraph 3.11.5, the "lot number for membrane filters and date received should be recorded." The Laboratory has records of this QC practice up to 1997, but not beyond. The practice should be re-established.

F. Although the Laboratory, pursuant to paragraph 3.14.2, is checking the calibration of each new lot of pre-calibrated test vessels (for Colilert test) and has produced a commendable record documenting this QC practice, it is recommended that the actual volume obtained be

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recorded instead of only a check mark. A record of actual volumes would provide raw data that could be assessed independently by other analysts, the microbiology supervisor, or the Laboratory QA officer, and therefore would represent better documentation. Long term trends in test vessel calibration could also be identified.

G. According to paragraph 4.4.3, "each batch of dilution/rinse water should be checked for sterility by adding 50 mL of water to 50 mL of a double strength non-selective broth (e.g., tryptic soy, trypticase soy, or tryptose broth)" and incubated at 35±0.5 °C for 24 hours. If growth occurs entire batch of dilution water should be discarded. At the time of the on-site visit, the Laboratory was not performing this QC sterility check. It is strongly recommended that this QC procedure be performed on all batches of dilution or rinse water, and the results recorded with the other media and dilution water preparation records. Note that if the 50 mL of non-selective broth is sterilized in a typical dilution bottle, the sterility check of the dilution or rinse water can be performed by pouring (with sterile technique) 50 mL of the water into the bottle containing the broth and incubating.

H. It is further recommended that, as matter of good laboratory practice, whenever the pH of a batch of media falls outside the acceptable range, the action taken (e.g., "batch discarded") and analyst's initials be recorded in the media prep log book.

I. Currently when performing the Colilert analysis, the 100 mL±2.5 mL sample test volume is obtained by carefully decanting 100 mL of the sample directly into the sterile IDEXX test vessel and subsequently comparing the volume in the test vessel against a second vessel clearly marked with the acceptable volume range (97.5-102.5 mL). It is recommended that this procedure be improved by doing the comparison at eye-level to make the best evaluation possible. Both bottles should be placed side by side on a platform fixed at eye-level. This recommendation follows what is generally accepted as good laboratory practice when reading any graduated measuring device, such as graduated cylinders or pipettes, i.e., they should always be read at eye-level.

J. Although the laboratory keeps detailed records of all analytical work, including the time an analysis begins, the time any subsequent analyses begins is not recorded. Paragraph 8.4.2 is understood to apply to any subsequent or additional analysis begun after the initial analysis. For example, if a positive MTF test is transferred to BGBB for confirmation, the time of the transfer should be recorded because the BGBB confirmatory test is a new analysis. Likewise if a positive MTF test is also transferred to EC medium for fecal coliforms, the time of transfer should be recorded because it marks the beginning of a new analysis. In other words, it is recommended that for the purpose of quality control, there should be documentation that all tests--presumptive, confirmatory, initial, subsequent, or otherwise--were incubated for the appropriate periods. Documentation on a batch by batch basis would be sufficient.

K. Similarly, it is recommended that for the Colilert analysis the time when the Colilert tests are

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read be recorded. This practice would be most important in those cases where a test, following the normal 24 hour incubation, is incubated for an additional 4 hours. The manufacturer cautions that a positive result (yellow color) after incubation for more than 28 hours is not a valid positive. Care should be taken not to incubate samples in excess of 28 hours. (See paragraph 5.6.5.)

L. At the present time, in order to neutralize residual chlorine in a sample, sample bottles are loaded with the appropriate amount of sodium thiosulfate prior to sterilization of the bottle. In addition, when performing the Colilert test, sample is poured into a sterile test vessel that also contains sodium thiosulfate in powdered form. Consequently, residual chlorine is probably being effectively neutralized in all samples analyzed with Colilert. However, with regard to the MTF method, it is possible that in some cases, excessive chlorination is not completely neutralized by the sodium thiosulfate in the sample bottle. It is recommended that a portion of these samples each month (e.g., 10%) be tested with a drop of iodine solution for excess sodium thiosulfate which will be present if all residual chlorine was neutralized. The iodine drop test could be easily performed (by a second analyst) on the sample water remaining in the collection bottle once the 100 mL test volume was removed. The sodium thiosulfate reacts with the iodine to produce sodium tetrathionate and sodium iodide both of which are colorless; consequently the amber color produce by the drop of iodine quickly disappears. If sodium thiosulfate is not present the amber color remains. A similar recommendation was made in 1996.

M. Currently water samples are collected in unmarked bottles and sent to the laboratory with the collection form wrapped around the bottle. Once the unmarked bottle containing the sample arrives in the laboratory, the identity of the bottle and sample depends entirely on the collection form staying with the sample. Because there is no unique identifier (such as a number) on the bottle, there is always the risk of losing the identity of the sample should the collection form and sample become separated. It is recommended that each sample bottle be marked (using an indelible ink marker) with a unique number that is recorded on the sample collection form by the collector. This procedure would insure that all collection information is clearly associated with a sample whether the collection form is kept with the sample or not.

V. Conclusions

The Laboratory's analysts are to be commended for their knowledge of methods and demonstrated commitment to a high level of quality control. Although the on-site evaluation is overall positive, it is recommended that due to the failure to analyze PE (Performance Evaluation) samples in 1999 (see deviation "B" above and Chapter III, p.III-7), the Laboratory's certification status be downgraded to "provisionally certified". Successful analysis of PE samples annually is an essential requirement (as is a favorable on-site evaluation) for maintaining full certification. If EPA receives confirmation that PE samples have been successfully analyzed for total coliform and fecal coliform (or *E. coli*) bacteria, and satisfactory corrective actions are

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developed for the other deviations, the Laboratory will be recommended for full certification under the Safe Drinking Water Act.

David E. Russell
Microbiological Evaluator

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Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Final Microbiology
SDWA Laboratory Evaluation Report
Rev. 2-21-00

Office of Laboratory Services
Department of Health and Human Resources
Bureau for Public Health
State of West Virginia

167 11th Avenue
South Charleston, WV 25303

On-site Evaluation Performed

on

Nov. 29 - Dec. 1, 1999

by

David E. Russell
Microbiological Evaluator

Office of Analytical Services and Quality Assurance
Environmental Science Center
U.S. Environmental Protection Agency, Region III
Ft. Meade, MD 20755-5350

I. Introduction

The microbiology laboratory is currently analyzing drinking and source water for total coliforms using Colilert (MMO-MUG), the Multiple-Tube Fermentation (MTF) technique (100 ml sample volume and bromocresol purple acid indicator), the Membrane Filtration (MF) technique, or Quanti-Tray, each followed by the appropriate procedures for fecal coliforms (or *E. coli*). Heterotrophic Plate Count (HPC) determinations are also performed on lab reagent water using the pour plate method.

Since the last EPA inspection in September of 1996, performance evaluation (PE) samples for total and fecal coliforms (or *E. coli*) have been successfully analyzed using Colilert, MTF, and MF methods in 1997 and 1998. The laboratory analytical staff should be commended for the analytical proficiency demonstrated by this record of PE analyses. PE samples were not analyzed in 1999.

The equipment and procedures employed in the bacteriological analyses of drinking water by this laboratory conform with the provisions of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA) , except as described in section III below.

II. Personnel

The following personnel currently analyze drinking and source water for total and fecal coliforms (or *E. coli*) using the Colilert, MTF (100ml volume), MF, or Quanti-Tray methods, and perform HPC analyses on lab reagent water:

Tom Ong
Joyce Vance-Abshire
Mike Flesher
Tracey Bossie
Joe Cochran
Micah Moore

The last three individuals listed have been at the state laboratory less than one year.

The inspector wishes to thank the Microbiology Supervisor, Microbiologists, and Lab Assistants for their cooperation and assistance during the on-site evaluation.

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III. Deviations

Deviations from the equipment and analytical procedures in the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA) are as listed below. Note that all chapter, page, or paragraph numbers and quotes are from the manual.

A. As stated in Chapter III (p.III-4), a laboratory analyzing drinking water should prepare a *written* description of its QA/QC activities (a QA plan), the purpose of which is to "ensure that routinely generated analytical data are scientifically valid and defensible, and are of known and acceptable precision and accuracy." QC procedures are to be specified in SOPs *written* for each method used. Furthermore, it is "the responsibility of the QA manager to keep the QA plan up to date". Although SOPs have been drafted for the Colilert and HPC methods, no SOPs exist for the MTF method (used daily to analyze drinking water) or the occasionally used MF and Quanti-Tray techniques. Nor are there written QA/QC procedures for the use and maintenance of laboratory equipment or general laboratory procedures common to all methods. Therefore, although a few of the elements exist in draft form, there is no complete comprehensive QA plan for drinking water microbiology.

B. Chapter III requires that laboratories, in order to maintain SDWA certification status, analyze PE samples annually. The purpose of this requirement is to confirm that the analytical proficiency of the laboratory is maintained over time despite changes in equipment and personnel that may occur. Although PE samples were successfully analyzed by the Laboratory in 1997 and 1998, none was analyzed in 1999. According to the manual (p. III-7), this omission alone is sufficient basis for downgrading certification status to "provisionally certified".

C. Paragraph 1.2(Chapter V) states that "before analyzing compliance samples, the analyst must demonstrate acceptable results for precision, specificity, and satisfactory analysis on unknown samples." Currently the Laboratory has no record of such a demonstration of analytical proficiency for each new analyst, although other records assessing analyst knowledge are being kept. Note that the above mentioned "unknown samples" could be prepared by the supervisor.

D. The Laboratory should be highly commended for it's practice of rejecting (without analysis) all *drinking water* samples that exceed the 30 hour holding time. *Source water*, however, has a sample holding time of 8 hours (paragraph 6.4 and Surface Water Treatment Rule, 40 CFR 141.74(a)), the purpose of which is to minimize changes in the sample's bacterial assemblage during the period between collection and analysis. Currently this holding time is regularly exceeded because *source water* samples are routinely analyzed the morning after the day they are collected. In addition negative results for the samples that have exceeded the holding time are not flagged as required by paragraph 8.3.5 (as modified in "Errata").

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IV. Recommendations

The following remarks are offered as suggestions to help improve the quality and integrity of the data the laboratory generates. Note that all paragraph numbers and quotes are from Chapter V of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA).

A. According to paragraph 3.1.5, all pH buffers used "should be dated upon receipt and when opened." Of the three buffer solutions (4.0, 7.0, 10.0) currently in use, two had only the date received marked on them and the third no dates at all. It is recommended as a matter of good laboratory practice that dates received and opened, and the initials of the analyst recording those dates, be marked on all pH buffers in use.

B. According to paragraphs 3.3.2, calibrations of glass and electronic thermometers should be checked annually against an NIST reference thermometer and the results recorded in a log book. Although considerable records of thermometer calibrations were available, they were not organized in such a way as to easily determine the history of calibration of individual thermometers. This problem had been already identified by the Laboratory and a new form or log sheet had been create, but was not yet in use at the time of the on-site visit. One of the new forms will be used for each thermometer; therefore, the record of calibrations for any one thermometer will be readily available. The Laboratory should be commended for this improvement in record keeping.

C. A further improvement in temperature record keeping would be to re-design the temperature recording tables to include the thermometer reading and the corrected temperature for each time the thermometer is read. When only the corrected temperature is recorded, there is no documentation that the analyst actually corrected the thermometer reading with the appropriate correction factor.

D. Regarding records kept for each autoclave, it is recommended that the autoclave for which the records are being kept be clearly indicated on the record form. Although the clip board with the autoclave records hangs next to the relevant autoclave, there is no association recorded on paper between the records and the autoclave.

E. According to paragraph 3.11.5, the "lot number for membrane filters and date received should be recorded." The Laboratory has records of this QC practice up to 1997, but not beyond. The practice should be re-established.

F. Although the Laboratory, pursuant to paragraph 3.14.2, is checking the calibration of each new lot of pre-calibrated test vessels (for Colilert test) and has produced a commendable record documenting this QC practice, it is recommended that the actual volume obtained be

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recorded instead of only a check mark. A record of actual volumes would provide raw data that could be assessed independently by other analysts, the microbiology supervisor, or the Laboratory QA officer, and therefore would represent better documentation. Long term trends in test vessel calibration could also be identified.

G. According to paragraph 4.4.3, "each batch of dilution/rinse water should be checked for sterility by adding 50 mL of water to 50 mL of a double strength non-selective broth (e.g., tryptic soy, trypticase soy, or tryptose broth)" and incubated at 35±0.5 °C for 24 hours. If growth occurs entire batch of dilution water should be discarded. At the time of the on-site visit, the Laboratory was not performing this QC sterility check. It is strongly recommended that this QC procedure be performed on all batches of dilution or rinse water, and the results recorded with the other media and dilution water preparation records. Note that if the 50 mL of non-selective broth is sterilized in a typical dilution bottle, the sterility check of the dilution or rinse water can be performed by pouring (with sterile technique) 50 mL of the water into the bottle containing the broth and incubating.

H. It is further recommended that, as matter of good laboratory practice, whenever the pH of a batch of media falls outside the acceptable range, the action taken (e.g., "batch discarded") and analyst's initials be recorded in the media prep log book.

I. Currently when performing the Colilert analysis, the 100 mL±2.5 mL sample test volume is obtained by carefully decanting 100 mL of the sample directly into the sterile IDEXX test vessel and subsequently comparing the volume in the test vessel against a second vessel clearly marked with the acceptable volume range (97.5-102.5 mL). It is recommended that this procedure be improved by doing the comparison at eye-level to make the best evaluation possible. Both bottles should be placed side by side on a platform fixed at eye-level. This recommendation follows what is generally accepted as good laboratory practice when reading any graduated measuring device, such as graduated cylinders or pipettes, i.e., they should always be read at eye-level.

J. Although the laboratory keeps detailed records of all analytical work, including the time an analysis begins, the time any subsequent analyses begins is not recorded. Paragraph 8.4.2 is understood to apply to any subsequent or additional analysis begun after the initial analysis. For example, if a positive MTF test is transferred to BGBB for confirmation, the time of the transfer should be recorded because the BGBB confirmatory test is a new analysis. Likewise if a positive MTF test is also transferred to EC medium for fecal coliforms, the time of transfer should be recorded because it marks the beginning of a new analysis. In other words, it is recommended that for the purpose of quality control, there should be documentation that all tests--presumptive, confirmatory, initial, subsequent, or otherwise--were incubated for the appropriate periods. Documentation on a batch by batch basis would be sufficient.

K. Similarly, it is recommended that for the Colilert analysis the time when the Colilert tests are

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read be recorded. This practice would be most important in those cases where a test, following the normal 24 hour incubation, is incubated for an additional 4 hours. The manufacturer cautions that a positive result (yellow color) after incubation for more than 28 hours is not a valid positive. Care should be taken not to incubate samples in excess of 28 hours. (See paragraph 5.6.5.)

L. At the present time, in order to neutralize residual chlorine in a sample, sample bottles are loaded with the appropriate amount of sodium thiosulfate prior to sterilization of the bottle. In addition, when performing the Colilert test, sample is poured into a sterile test vessel that also contains sodium thiosulfate in powdered form. Consequently, residual chlorine is probably being effectively neutralized in all samples analyzed with Colilert. However, with regard to the MTF method, it is possible that in some cases, excessive chlorination is not completely neutralized by the sodium thiosulfate in the sample bottle. It is recommended that a portion of these samples each month (e.g., 10%) be tested with a drop of iodine solution for excess sodium thiosulfate which will be present if all residual chlorine was neutralized. The iodine drop test could be easily performed (by a second analyst) on the sample water remaining in the collection bottle once the 100 mL test volume was removed. The sodium thiosulfate reacts with the iodine to produce sodium tetrathionate and sodium iodide both of which are colorless; consequently the amber color produce by the drop of iodine quickly disappears. If sodium thiosulfate is not present the amber color remains. A similar recommendation was made in 1996.

M. Currently water samples are collected in unmarked bottles and sent to the laboratory with the collection form wrapped around the bottle. Once the unmarked bottle containing the sample arrives in the laboratory, the identity of the bottle and sample depends entirely on the collection form staying with the sample. Because there is no unique identifier (such as a number) on the bottle, there is always the risk of losing the identity of the sample should the collection form and sample become separated. It is recommended that each sample bottle be marked (using an indelible ink marker) with a unique number that is recorded on the sample collection form by the collector. This procedure would insure that all collection information is clearly associated with a sample whether the collection form is kept with the sample or not.

V. Conclusions

The Laboratory's analysts are to be commended for their knowledge of methods and demonstrated commitment to a high level of quality control. Although the on-site evaluation is overall positive, it is recommended that due to the failure to analyze PE (Performance Evaluation) samples in 1999 (see deviation "B" above and Chapter III, p.III-7), the Laboratory's certification status be downgraded to "provisionally certified". Successful analysis of PE samples annually is an essential requirement (as is a favorable on-site evaluation) for maintaining full certification. If EPA receives confirmation that PE samples have been successfully analyzed for total coliform and fecal coliform (or *E. coli*) bacteria, and satisfactory corrective actions are

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developed for the other deviations, the Laboratory will be recommended for full certification under the Safe Drinking Water Act.

David E. Russell 2/22/00

David E. Russell Date
Microbiological Evaluator

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From: <Martin.Ted@epamail.epa.gov>
To: R3MD1.R3CRL(COSTAS-ROBIN)
Date: 12/16/99 3:55pm
Subject: Re: SDWA question -Forwarded

ICP-AES instrument performance between solutions containing acid concentrations of 2%+2%, 2%+1%, or 1% HNO3 should be non-detectable. Remember the sample preparation is intended to be uniform and applicable to ICP-MS and STGFAA as well as ICP-AES. The final acid concentrations following digestion were dictated by the ICP-MS technique not ICP-AES. In Method 200.7 sections 7.9, 11..11, and 11.2.1 are very specific, can be followed without differences in analytical performance. Whether his operating procedure is considered a deviation is your call. If he can demonstrate acceptable performance, it may more a legal question than a technical question.

The concern in section 9.3.4 is an RDS of less than 3%. If that can be achieve with 3 integrations, that should be acceptable.

I hope these answers are of some help.

Have a Merry Christmas. Ted.

Robin Costas@EPA on 12/16/99 12:53:29 PM

To: Ted Martin/CI/USEPA/US@EPA
cc:
Subject: SDWA question -Forwarded

Ted, I am sending you a message that I sent earlier to Jack but I have a feeling he is on vacation. If you can help me out, I would appreciate it. Thanks!

Date: Fri, 03 Dec 1999 11:42:10 -0500
From: ROBIN COSTAS <COSTAS.ROBIN@EPAMAIL.EPA.GOV>
To: CREED.JACK@EPAMAIL.EPA.GOV
Subject: SDWA question
Mime-Version: 1.0
Content-Type: text/plain
Content-Disposition: inline

Hi Jack, hope you had a good Thanksgiving! I

FAX 304-558-4143

have 2 short questions for you. I just came back from an SDWA inspection on the state of W.Virginia and this issue came up. The analyst is very conciencious about matching his standard matrix to the digested sample matrix for ICP (200.7ver 4.4). He insists that if the standards are supposed to be 2%nitric and 2%HCl, then he must digest the samples the same way. My feeling was that in ICP, the differences between 1% and 2% acid concentrations was not significant, so the 2%2% standards would be adequate for water samples (2%1%) and soil samples (2%2%). Is that your feeling also, or am I way "off-base" here? And, if so, how do we handle the standards for "direct analysis" and dissolved analyte digestion...which have no HCl in them?
So, I guess the basic question is: if the lab is not preparing the samples and standards exactly as described in the method, do you consider this a deviation from the method, which I need to write them up on?

Also, Section 9.3.4 says that the RSD for the IPC must be <3% from replicate integrations > or equal to 4. This seems to infer that the entire run must be run using 4 integrations since you would not be able to switch to 4 for just one sample. I have always run with only 3 integrations. How do you handle this issue?
Thanks so much for your help. Robin.

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

STATE OF WEST VIRGINIA
DEPARTMENT OF HEALTH AND HUMAN RESOURCES

Cecil H. Underwood
Governor

Joan E. Ohl
Secretary

MEMORANDUM

DATE: April 28, 1999

TO: Marcy Mair

FROM: Frank W. Lambert, Jr., Dr. P.H., Director
Office of Laboratory Services

SUBJECT: **JOE SLAYTON'S VISIT**

DIRECTIONS TO WEST VIRGINIA STATE HYGIENIC LABORATORY

Hygienic Lab:

Westbound on I-64: Exit Montrose Drive (Exit 56), proceed north to MacCorkle Avenue, turn left, proceed west and turn right onto "D" Street, at Suzie's Hamburgers. Follow road along river to laboratory (167 11th Avenue).

Environmental Chemistry Lab:

The Environmental Chemistry laboratory is at Big Chimney on I-79. It will be best if we take you there from the State Hygienic Laboratory.

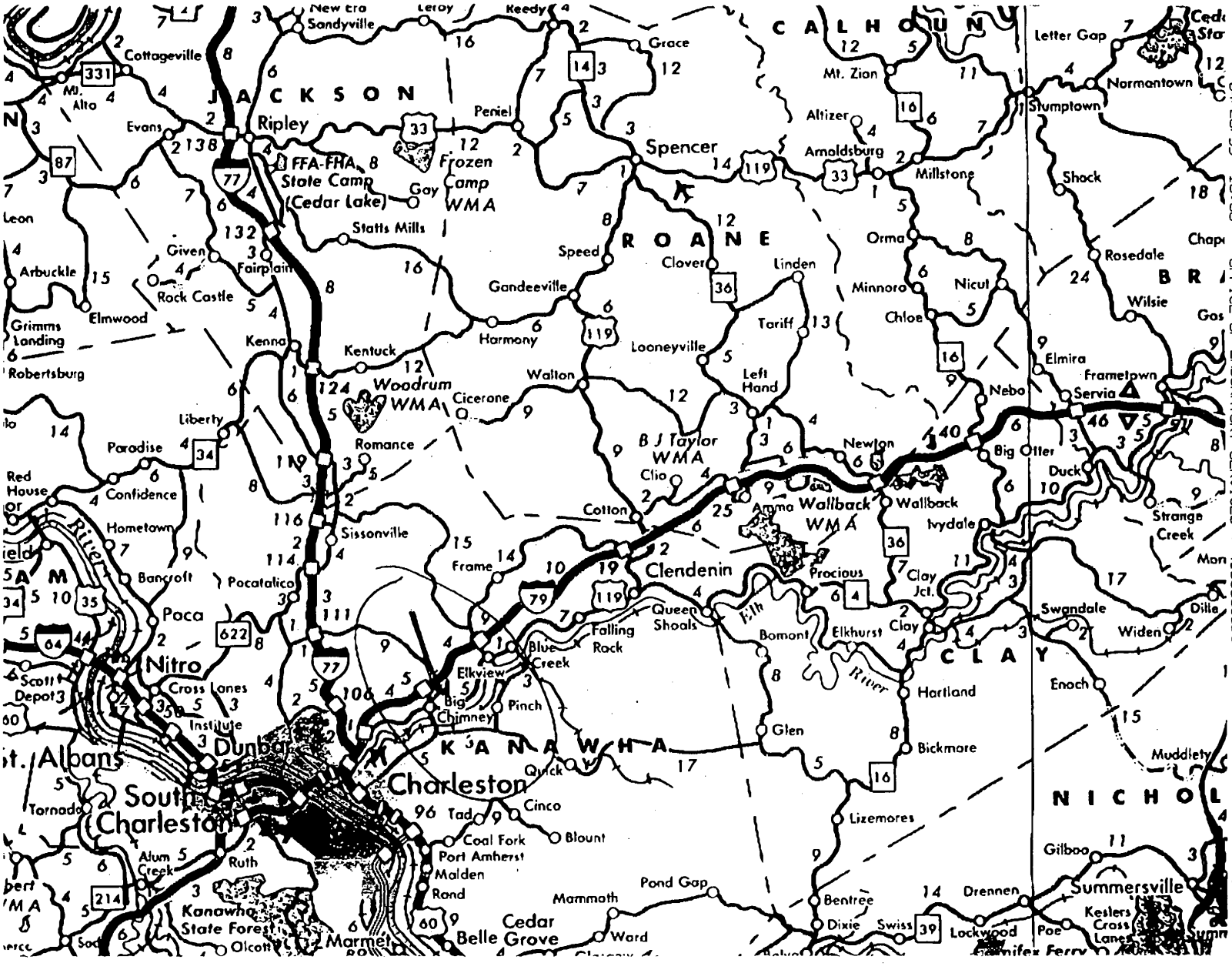
MOTELS

Both the RAMADA INN at 400 2nd Avenue, South Charleston (Exit 56) (304-744-4641) or the Red Roof Inn at 4006 MacCorkle Ave., S.W. (I-64 exit 54) (304-744-1500) are close to the State Hygienic Laboratory.

The enclosed maps may help you locate these places. If you have questions, please call (304) 558-3530.

Enclosures

BUREAU FOR PUBLIC HEALTH
OFFICE OF LABORATORY SERVICES
167 11th Avenue
South Charleston, West Virginia 25303-1137
Phone: (304) 558-3530 FAX: (304) 558-2006



04/28/99 15:38 OFFICE OF LABORATORY SERVICES → 4103053095 NO.124 P003/004

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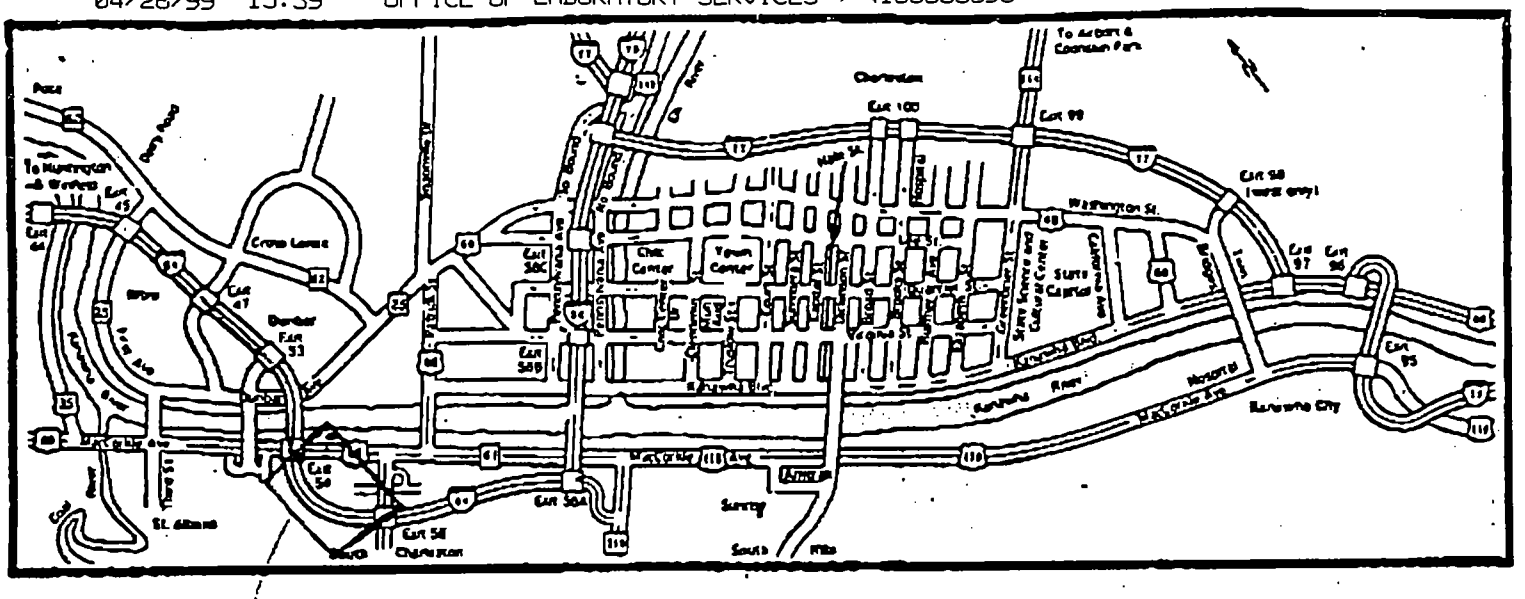
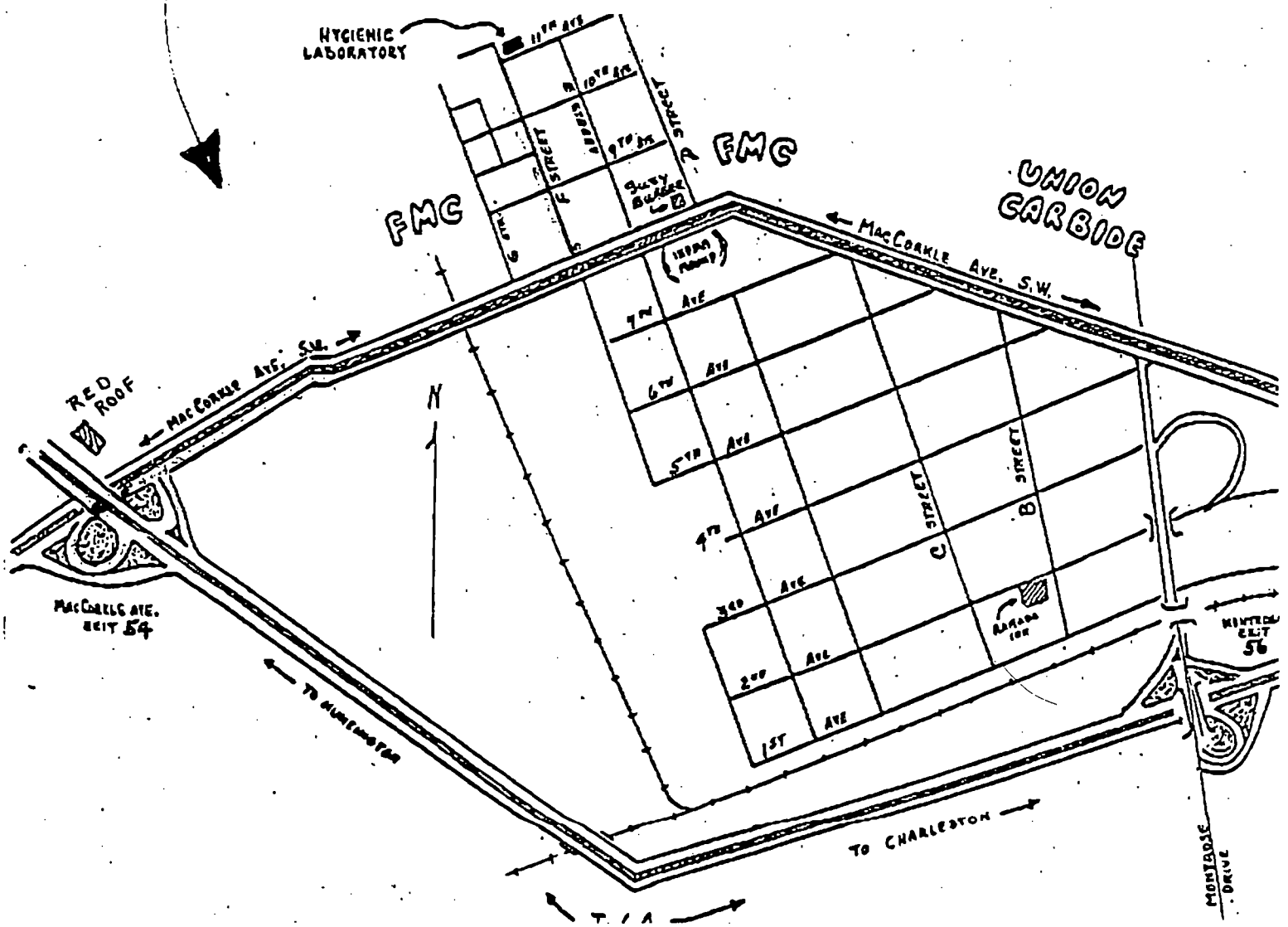


To get to the State Hygienic Laboratory
when entering South Charleston:

Southbound on I-77 or I-79, take "I-64 West-Huntington" and exit at Montrose Drive.
Eastbound on MacCorkle Avenue: Turn left at "F" Street.
Eastbound on I-64: Exit at MacCorkle Avenue, proceed East, and turn left at "F" Street.
Westbound on MacCorkle Avenue: Turn right at "D" Street, at the Burger Chef.
Westbound on I-64: Exit at Montrose Drive, proceed North to MacCorkle Avenue, turn left, proceed west and turn right onto "D" Street, at SUZIE'S HAMBURGERS



Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

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Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

STATE: West Virginia Last Up-Date December 31, 2002

LABORATORY PROFICIENCY TESTING (PT) SAMPLE PERFORMANCE & LATEST ON-SITE REVIEW

C - Certified	PC - Provisionally Certified	IC - Interim Certified
NC - Not Certified	A - Acceptable	NA - Not Acceptable
ND - No Data Submitted	AP - Approved	NP - Not Approved

INORGANIC CHEMICALS

CONTAMINANT	2002							
	OVERALL CERTIFICATION		PT SAMPLES				ON-SITE REVIEW 11/30/99	
		Method	A	NA	ND	Method		Method
Antimony	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Arsenic	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Barium	C	EPA200.7	X			EPA200.7	C	EPA200.7
Beryllium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Cadmium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Chromium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Copper	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Cyanide	NC	SM 4500 CN F	X			SM 4500 CN F		
Fluoride	C	EPA300.0	X			EPA300.0	C	EPA300.0
Lead	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Mercury	C	EPA245.1	X			EPA245.1	C	EPA245.1
Nitrate	C	EPA353.2	X			EPA353.2	C	EPA353.2
Nitrite	C	EPA353.2	X			EPA353.2	C	EPA353.2
Selenium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Thallium	C	EPA200.9	X			EPA200.9	C	EPA200.9
Chloride	AP	EPA300.0	X			EPA300.0	AP	EPA300.0
Sulfate	AP	EPA300.0	X			EPA300.0	AP	EPA300.0
TDS	NP	EPA160.1			X	EPA160.1	AP	EPA160.1

	NP	SM2540C	X			SM2540C		
	NP	SM2540C	X			SM2540C		
Manganees	NP	SM 3111 B	X			SM 3111 B		
Nickle	NP	SM 3111 B	X			SM 3111 B		
Zinc	NP	SM 3111 B	X			SM 3111 B		

ORGANIC CHEMICALS

CONTAMINANT	2002							
	OVERALL CERTIFICATION		PT SAMPLES				ON-SITE REVIEW	
		Method	A	NA	ND	Method		Method
Chloroform	NC							
Bromodichloromethane	NC							
Bromoform	NC							
Chlorodibromomethane	NC							
Total Trihalomethanes	NC							
Vinyl Chloride	NC							
Benzene	NC							
Carbon tetrachloride	NC							
1,2-Dichloroethane	NC							
Trichloroethylene	NC							
para-Dichlorobenzene	NC							
1,1-Dichloroethylene	NC							
1,1,1-Trichloroethane	NC							
cis-1,2-Dichloroethylene	NC							
1,2-Dichloropropane	NC							
Ethylbenzene	NC							
Monochlorobenzene	NC							

ONPG-MUG Test (Colilert)	C	SM9223	X			SM9223	C	SM92223
Heterotrophic Plate Count (On-Site Only)	C						C	SM9215B

LEAD AND COPPER RULE

CONTAMINANT	2002							
	OVERALL CERTIFICATION		PT SAMPLES				ON-SITE REVIEW 11/30/99	
		Method	A	NA	ND	Method		Method
Lead	C	SM3113B	X			SM3113B	C	SM3113B
Copper	C	SM3113B	X			SM3113B	C	SM3113B
pH	NC	EPA150.1	X			EPA150.1		
Conductivity	NC	SM2510B	X			SM2510B	NC	SM2510B
Calcium or Calcium Hardness as $CaCo_3$	NC	SM3500 CAD	X			SM3500 CAD		
Alkalinity	NC	SM2320B	X			SM2320B		
Orthophosphate	NC							
Silica	NC							
Temperature (On-Site Only)	NC							
Sodium	C	SM3111B	X			SM3111B	C	SM3111B
Turbidity	C	EPA180.1	X			EPA180.1	C	EPA180.1

Ex. 5 - Deliberative

WVA 2003

Title 40 Part 141 and Part 143
SDWA requirements for Certification of Metals
January 2002

***Primary** Contaminants with MCL values (141.62):*
Shall be analyzed to determine compliance with the MCLs listed in 141.62. The MCL for arsenic will become 0.010 mg/L on January 23, 2006. Must use methods in table 141.23(k)(1).

	Parameter	IDC	Calibration Standards(~~mg/L~~ ppb)	RL	MCL(mg/L)		MDL(mg/L)*	Digested
18th 3113B	Antimony	✓	Blk; 3, 6, 12	3	0.006	6	.84 ppb	✓
3113B	Arsenic	✓	Blk; 2, 5, 10, 20	2	0.01	10	1.05 "	✓
200.7	Barium	✓	Blk; 0.5, 5, 10 ppm	.005	2	2	.0003	✓
3113B	Beryllium	✓	Blk; 0.2, 0.5, 1, 2	0.2	0.004	4	0.05 ppb	✓
3113B	Cadmium	✓	Blk; 1, 2, 4	1	0.005	5	0.12 ppb	✓
3113B	Chromium	✓	Blk; 1, 2.5, 5, 10	1	0.1	100	0.51 ppb	✓
245.1	Mercury	✓	Blk; RL .0002, .0005, .0010, .0020 ppm; 0.2, 0.5, 1, 2 ppb 0.2		0.002	2	0.064 ppb	✓
3113B	Selenium	✓	Blk; 2, 5, 10	2	0.05	50	1.01 ppb	✓
200.9	Thallium	✓	Blk; 2, 4, 8	2	0.002	2	0.65 ppb	no

(*MDL - fill in laboratory values for comparison)

***Primary** Contaminants with PQL levels (141.89):*
*SubPart I of 141 - Lead and Copper Rule - If either Pb or Cu exceeds the Action Level, then water system must implement treatment procedure which includes analyzing **calcium** for hardness and **silica** when a silicate compound has been added to the water. Must use methods in table 141.23(k)(1).*

	Parameter	IDC	Calibration Standards(~~mg/L~~ ppb)	RL	AL / PQL(mg/L)*		MDL(mg/L)*	DIP
3113B	Copper	✓	Blk; 1, 2.5, 5, 10	1	1.3 / 0.050	50	0.32 ppb	✓
3113B	Lead	✓	Blk; 1, 2.5, 5, 10	1	0.015 / 0.005	15/5	0.24 ppb	✓

*AL = Action Level
*PQL = Practical Quantitation Limit
*Must report values as measured between PQL and MDL or ½ PQL.

***Primary** Contaminants for special monitoring - no MCL (141.41):*
Water system must be analyzed for Na at least once a year and reported to EPA. Must use methods in table 141.23(k)(1).

	Parameter	IPL	RL	Calibration Standards(mg/L)	recommended MCL	MDL(mg/L)	DIS
3111	Sodium	✓	2	Blk; 2, 5, 10, 15, 20	20 ppm	0.08 ppm	✓

*Optional **Primary** Contaminants which must be certified if they are to be reported - no MCL (141.23(k)(3)):*
These are to be listed as a primary if they are to be certified.

	Parameter	IPL	RL	Calibration Standards(mg/L)	MDL(mg/L)	DIS
	Calcium			Blk;		
3113B	Nickel	✓	2	Blk; 2, 5, 10, 20 ppb	0.62 ppb	✓
	Magnesium			Blk;		
	Silica			Blk;		

***Secondary** Contaminants - primarily affect aesthetic quality unless very high concentrations. Can use any method and they don't need to be certified (Part 143). Report as Acceptable or Not. "The regulations are not Federally enforceable but are intended as guidelines for the states." (SMCL table - 143.3.)*

	Parameter	IPL	RL	Calibration Standards(mg/L)	SMCL (mg/L)	MDL(mg/L)	DIS
3113B	Aluminum		3	Blk; 3, 15, 30 ppb	0.05-0.2	2.14 ppb	✓
	Copper *(also a primary)*			Blk;	1.0		
3111	Iron	✓	.05	Blk; 0.05, 0.1, 0.25, 0.5, 0.06 ppm	0.3	0.014 ppm	✓
3111	Manganese	✓	.02	Blk; .02, .05, .1, .25, .5 ppm	0.05	0.009 ppm	✓
3113B	Silver	✓	0.5 ppb	Blk; ppb .5, 1.25, 2.5, 5 ppb	0.1	0.22 ok	✓
3111	Zinc	✓		Blk; .02, .05, .1, .25, 5 ppm	5.0	0.009 ppm	✓

G:\DATA\SHARED\WP\A Team\FORMS\METALS\SDWA primary and secondary rules 2.wpd

WEST VIRGINIA
DEPARTMENT OF HEALTH AND HUMAN RESOURCES
OFFICE OF LABORATORY SERVICES
ENVIRONMENTAL CHEMISTRY LABORATORY

FACSIMILE TRANSMITTAL SHEET

TO: Robin Costas	FROM: Larry Duffield
COMPANY: EPA Region Three	SECTION:
FAX NUMBER: 410-305-3093	DATE: July 2, 2003
PHONE NUMBER:	TOTAL NO. OF PAGES INCLUDING COVER: 5
RE:	

☐ URGENT ☒ FOR REVIEW ☐ PLEASE COMMENT ☐ PLEASE REPLY ☐ PLEASE RECYCLE

NOTES/COMMENTS:

Message: Robin, here is a copy of the data report of the IDC for Aluminum as require. The known reference for this test is the same as is used for the daily Quality Control Sample which is an EPA Performance Evaluation WS034-1 diluted to 10X. For the IDC, four 35 mℓ aliquots were digested in polyproplylene tubes in a 5.2% HNO_3 Acid Matrix just like regular unknown samples along with a LRB and LFB for the batch. They recovered within ±10% of True Value which is 15.1 ppb.% RSD between replicates was 1.45%. A copy will be kept on file for future review. Thanks.

4710 CHIMNEY DRIVE SUITE G, CHARLESTON, WEST VIRGINIA 25302
PHONE: (304)558-0197 FAX: (304) 558-4143

Freedom_0006095_0163

Aluminum
IDC Test

BLANK QC	0.00		-0.088	-0.088 01Jul03 09:19 CONCENTRATION LESS THAN IDL	
BLANK QC	0.00		-0.002	-0.002 01Jul03 09:21 CONCENTRATION LESS THAN IDL	
STANDARD 2 QC	15.00	0.0	0.106	0.106 01Jul03 09:23	
STANDARD 2 QC	15.00	0.0	0.108	0.108 01Jul03 09:25	
STANDARD 2 QC	15.00	0.0	0.103	0.103 01Jul03 09:27	%RSD=3.12%
STANDARD 2 QC	15.00	0.0	0.100	0.100 01Jul03 09:29	
STANDARD 2 QC	15.00	0.0	0.107	0.107 01Jul03 09:31	
BLANK QC	0.00		0.009	0.009 01Jul03 09:33 CONCENTRATION LESS THAN IDL	

Freedom_0006095_0164

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR LARRY A. DUFFIELD
DATE JULY 01, 2003
BATCH A1

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 35 Al 3.00-30.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK AREA
LAMP POSITION	8
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	309.3
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	32.0	3.0	ALTERNATE	NO
2	130	6.0	3.0	ALTERNATE	NO
3	150	7.0	3.0	ALTERNATE	NO
4	1400	5.0	3.0	ALTERNATE	NO
5	1400	8.0	3.0	ALTERNATE	NO
6	1400	1.0	3.0	NORMAL	NO
7	1400	1.0	0.0	NORMAL	NO
8	2525	1.0	0.0	NORMAL	YES
9	2525	3.0	0.0	NORMAL	YES
10	2550	3.0	3.0	NORMAL	NO
11	2575	2.0	3.0	NORMAL	NO

Freedom_0006095_0165

SAMPLER PARAMETERS

VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	24	14
STANDARD 1	2	22	14
STANDARD 2	10	14	14
STANDARD 3	20	4	14
SAMPLE	20	4	14

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 95
INJECT RATE 1

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	15.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	4
QC SPIKE CONCENTRATION	30.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	1.16 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Al :

Maximum Ash Temperature : 1400 xC
Recommended Atomize Temperature : 2500 xC

Response with Argon :
10 microlitres of 30 micrograms/litre gives about 0.2 ABS.
PMV= 298.3 METHOD: SM 3113 B
MODIFIER: 800 mg/l Pd + Mg + H2
QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.00 PPB
NV= NOT VALID
RL= REPORTING LIMIT= 0.003 PPM
IDL= 0.75 PPB 11-2-00 3DAY MEAN
MDL= 2.01 PPB 10-16-02 3DAY MEAN LDR= 50.0 PPB 12-05-00

Freedom_0006095_0166

BLANK QC	0.00		0.041	0.041 01Jul03 09:38 CONCENTRATION LESS THAN IDL		
BLANK QC	0.00		0.008	0.003 01Jul03 09:44 CONCENTRATION LESS THAN IDL	0.011	0.009
STANDARD 1 QC	3.00	11.4	0.021	0.020 01Jul03 10:22	0.024	0.020
STANDARD 2 QC	15.00	3.3	0.098	0.097 01Jul03 10:28	0.095	0.102
STANDARD 3 QC	30.00	1.4	0.186	0.185 01Jul03 10:35	0.185	0.189

r = .9997

QCSTANDARD QC	15.44	3.1	0.100	0.097 01Jul03 10:41	0.101	0.103
QC BLANK QC	-0.26	0.0	-0.002	-0.002 01Jul03 10:44 CONCENTRATION LESS THAN IDL		
WS034-1 10X QC	13.89	0.0	0.091	0.091 01Jul03 10:47		
LAB RE BLANK QC	-0.37	0.0	-0.003	-0.003 01Jul03 10:49 CONCENTRATION LESS THAN IDL		
RLV-3.00 PPB QC	3.00	0.0	0.021	0.021 01Jul03 10:56		
LFB-25.0 PPB QC	26.12	0.0	0.164	0.164 01Jul03 10:59		
QCSTANDARD QC	15.90	0.0	0.103	0.103 01Jul03 11:01		
QC BLANK QC	0.03	0.0	0.000	0.000 01Jul03 11:03 CONCENTRATION LESS THAN IDL		
#1 WS034-1 10X QC	15.57	0.0	0.101	0.101 01Jul03 11:06		
#2 WS034-1 10X QC	15.05	0.0	0.098	0.098 01Jul03 11:08		
#3 WS034-1 10X QC	15.35	0.0	0.100	0.100 01Jul03 11:15		
#4 WS034-1 10X QC	15.20	0.0	0.099	0.099 01Jul03 11:17		
QCSTANDARD QC	14.19	0.0	0.093	0.093 01Jul03 11:22		
QC BLANK QC	-0.16	0.0	-0.001	-0.001 01Jul03 11:24 CONCENTRATION LESS THAN IDL		

Daily QCS %R = 92.0 T.V. = 15.1

%R = 100.0

%R = 104.5

%R = 106.0

Note: For IDC T 4 aliquots of WS034-1 10X use daily QCS Dig and analyzed Precision + Accu 2D

%RSD = 1.45%

$\bar{X}$ = 15.30

T.V. = 15.1 ppb

Lab #	Method/ Digestion Type	Block Temp.	LR Blank Dig.?	LFB Dig.?	Date Acidified	pH <2 ?	Date Digested	Dig. Vol Checked	Chem.
030127	SM3113B	100°C	Yes	Yes	5-29-03	Yes	6-4-03	Yes	[illegible]
030128	5.2% HNO3								
030133					6-2-03				
030133DUP									
030133LFM									
030134					6-3-03				
030134DUP									
030134LFM									
030140	SM3111B	100°C	Yes	Yes	6-5-03	Yes	6-6-03	Yes	[illegible]
030140DUP	5.2% HNO3								
030140LFM									
030148	SM3113B	100°C	Yes	Yes	6-17-03	Yes	6-26-03	Yes	[illegible]
030148DUP	5.2% HNO3								
030148LFM									
030141	SM3113B	100°C	Yes	Yes	6-11-03	Yes	6-27-03	Yes	[illegible]
030145	5.2% HNO3				6-13-03				
030146									
030146DUP									
030146LFM									
030147					6-17-03				
030152					6-26-03				
030145	SM3113B	PS: 100°C	Yes	Yes	6-13-03	Yes	6-30-03	Yes	[illegible]
030146	1.22% HNO3 + 2.0% H2O2								
030146DUP									
030146LFM									
5034-110x#1	SM3113B	100°C	Yes	Yes	6-27-03	Yes	6-30-03	Yes	[illegible]
5034-110x#2	5.2% HNO3								
5034-110x#3									
5034-110x#4									

(from Digestion Log Book)

4 replicates of QCS for Al IDC test

WEST VIRGINIA
DEPARTMENT OF HEALTH AND HUMAN RESOURCES
OFFICE OF LABORATORY SERVICES
ENVIRONMENTAL CHEMISTRY LABORATORY

FACSIMILE TRANSMITTAL SHEET

TO: Robin Costas	FROM: Larry Duffield
COMPANY: EPA Region Three	SECTION:
FAX NUMBER: 410-305-3093	DATE: July 2, 2003
PHONE NUMBER:	TOTAL NO. OF PAGES INCLUDING COVER: 6
RE:	

☐ URGENT ☒ FOR REVIEW ☐ PLEASE COMMENT ☐ PLEASE REPLY ☐ PLEASE RECYCLE

NOTES/COMMENTS:

Message: Robin, here is a copy of the data report of the IDC for Aluminum as require. The known reference for this test is the same as is used for the daily Quality Control Sample which is an EPA Performance Evaluation WS034-1 diluted to 10X. For the IDC, four 35 mℓ aliquots were digested in polyproplylene tubes in a 5.2% HNO_3 Acid Matrix just like regular unknown samples along with a LRB and LFB for the batch. They recovered within ±10% of True Value which is 15.1 ppb 0% RSD between replicates.

From: Ex. 6 - Personal Privacy
To: <larryduffield@wvdhhr.org>
Date: 6/24/03 6:02AM
Subject: Water - At Risk If You Drink It?

<map name="Map">

****
Is there someone you know who would benefit from the information in these dispatches? Please forward this dispatch to them and have them visit my Web site at http://doctorspreferred.com/Apps/DCS/mcp?r=70042nHd41LZT0120003ICA042nHd0mYBFcYB3R
****
****
News to Use in this Dispatch:

* Water - At Risk If You Drink It?
* Genetically Engineered Rain
* By-the-Way... "No to Chlorine!"
* Distill My Heart, Distill

Water - At Risk If You Drink It?

We Have Two Circulation Systems?

Dear Friend:

As you know, I've been pretty outspoken when it comes to the contamination of our drinking water and the importance of using only distilled water. (http://doctorspreferred.com/Apps/DCS/mcp?r=70042nHd41LZT0120003ICJ042nHd0mYBFcYB3R) Over the years, I've covered research concerning the estrogen-like chemical pesticides reaching our groundwater and their direct relationship to the increase in female breast cancer. I've described how chlorinated drinking water has been shown to be the primary cause of bladder cancer. And I've uncovered the frightening truth about the high levels of lead in school water supplies and their link to permanent behavioral problems and learning disabilities in our children.

Just when I thought I'd heard the worst about the dangers of our drinking water, I got a call from a research scientist detailing even greater horrors, which leads me to ask the question; do you remember when you were a kid and stood in the rain trying to catch raindrops on your tongue? It's definitely not a good idea anymore.

Stephen Muller, a chemist at the Swiss Federal Institute for Environmental Science and Technology, reported that much of rainwater today is contaminated with crop pesticides. It seems that common pesticides like atrazine, alachlor, and others evaporate after being applied to crop fields and then combine with the water vapor in clouds. When the vapor falls as rain, the pesticides come right back down to Earth, but this time they're not just in the fields. They're everywhere. These pesticides are particularly concentrated in rain that falls a few minutes after crops have been sprayed; so concentrated, in fact, that it would be illegal to supply this rain as drinking water.

In the European Union and Switzerland, laws require that drinking water contain no more that 100 nanograms of pesticides per liter of water. In their tests of rain samples from 41 different storms, nine contained more that 100 nanograms of atrazine (a common herbicide) per liter, one had 900 nanograms and one had 4,000 nanograms per liter of 2,4-dinitrophenol (another common pesticide). The problem isn't just limited to Europe or Switzerland.

Genetically Engineered Rain

Research conducted in Sweden linked pesticide exposure http://doctorspreferred.com/Apps/DCS/mcp?r=70042nHd41LZT0120003ICH042nHd0mYBFcYB3R to non-Hodgkin's lymphoma--one of the most rapidly increasing cancers in Western countries. The incidence of non-Hodgkin's lymphoma has risen by 73% since 1973 in the United States alone. The Swedish researchers found that both Americans and Europeans who contracted the cancer were 2.3 times more likely to have been exposed to the herbicide glyphosate than individuals who never developed the cancer. The researchers report that glyphosate and other common pesticides suppress the immune system and trigger the formation of cancer.

For those who may not be avid farmers or gardeners, let me give you some background. Glyphosates are nonselective, systemic chemicals used in popular weed killers like Roundup. They kill plants from the inside-out by preventing them from making food through photosynthesis. But because glyphosates kill indiscriminately farmers can't just spray them across their fields or they'll lose precious crops along with the weeds. For this reason, Monsanto created what they referred to as "Roundup-Ready" seeds. These are patented crop seeds genetically modified to withstand high doses of glyphosate that would otherwise destroy them along with weeds. Based on the popularity of these seeds, it looks like we'll continue to see more glyphosate in our rain and drinking water--and based on this recent European research, we'll be seeing a lot more cases of lymphoma and other illnesses linked to pesticide exposure.

So now we have genetically modified rain to grow genetically modified crops. No wonder scientists want to genetically modify people. At least they're consistent. I just wonder if scientists couldn't be genetically modified so they wouldn't want to genetically modify everything else anymore. That's one modification I'd consider endorsing.

By-the-Way... "No to Chlorine!"

Every time I talk about the dangers of drinking water, I get several letters saying that our chlorinated drinking water is some of the best in the world. Let me make a few points on this subject:
* First, chlorine offers no protection whatsoever against pesticides (such as Roundup and the others I discussed above) or viruses or other non-bacterial contaminants.
* Second, chlorine breaks down into a compound called trihalomethane which has been linked to increased cancer rates and a higher risk of stillbirth in pregnant mothers (Epidemilogy 99;10:23-237).
* The only benefit to adding chlorine to drinking water is to eliminate harmful bacteria such as E. coli and salmonella. Which brings me to my third point: Research data suggest that chlorine isn't 100% effective on the bacteria front, either.

For some time the bacteria Helicobacter pylori (H. pylori) has been implicated in practically every ailment of the gastrointestinal tract, including ulcers, stomach inflammation, and even cancer. The fact that at least half of all individuals have H. pylori naturally living in their guts makes it appear to be the likely culprit in these ailments. But until recently no one has been able to find an external reservoir for the bacteria. Researchers in Scotland recently informed us that H. pylori can be found thriving in the sticky biofilm that naturally develops inside water pipes.

Chlorine passing through water pipes only kills the top layer of bacteria. As the chlorine gets used up in the process, live H. pylori bacteria from lower layers of the biofilm get washed away into the water, either in small amounts or large clumps. The problem may be even worse in unchlorinated water coming from private wells.

Distill My Heart, Distill

If you have any gastrointestinal problems whatsoever, it would be worth your while to switch to distilled water. In fact that recommendation goes for everyone, regardless of your current health status, or even the quality of your local water supply. Years ago, I suggested various purification methods based on certain factors such as proximity to agricultural communities. But the research on "cloud pollution" and

high levels of pesticides in rainwater has rendered locally specific contaminants a thing of the past. You may not live near any farmers using Roundup-Ready seeds and Roundup, but I would strongly suspect you're living with Roundup (glyphosate)-tainted water...

I've been recommending distillation for many years and today I feel more strongly than ever that it's the only way to go when it comes to purifying your water. There is no other method that removes all types of contaminants and leaves you with water the way nature intended: two parts hydrogen, one part oxygen. Water just doesn't get any purer than that.

Till next time,

Ex. 6 - Personal Privacy

PS: In the July issue of Alternatives I discuss aging and taste. You'll discover the importance of smell in the taste process. You'll want to read this article if you have noticed that as you've gotten older you're adding salt, pepper, and other spices to your food in greater quantities. I'll provide an answer to the problem I found in Europe. You won't want to miss this information and if you http://doctorspreferred.com/Apps/DCS/mcp?r=70042nHd41LZT0120003ICB042nHd0mYBFcYB3R by July 9 your subscription will begin with this issue.

****

Ex. 6 - Personal Privacy is a medical investigator, international traveler, and one of the world's leading authorities in natural healing. Often years ahead of the conventional medical establishment, he has located, evaluated, and announced effective treatments and cures for practically every major health concern today. He shares these breakthroughs with over 250,000 insiders through his in-depth monthly newsletter Alternatives.

To learn more about Ex. 6 - Personal Privacy and the values underlying what he does each month in Alternatives, visit his Web site.

Ex. 6 - Personal Privacy

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You are receiving this email at larryduffield@wvdhhr.org because you indicated an interest in receiving special updates and offers from Ex. 6 - Personal Privacy We hope you'll find these updates interesting and informative. But if you'd rather not receive them, simply send a message to Ex. 6 - Personal Privacy Please be advised that this process may take 5-7 business days for your email address to be removed from all of our mailing lists. We apologize for any inconvenience this may cause.

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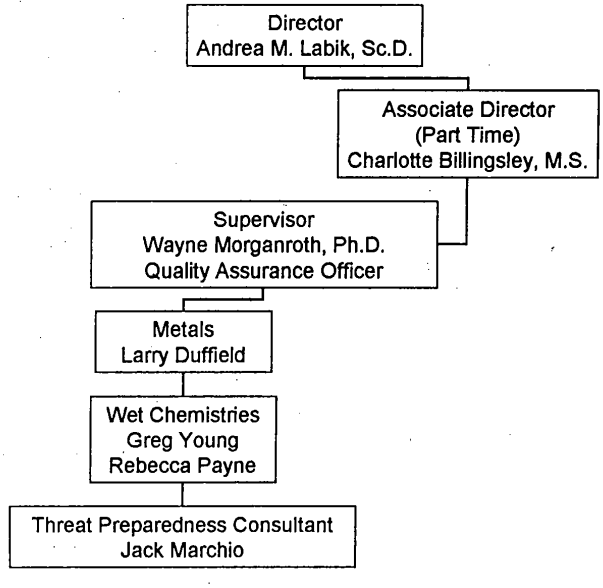
WEST VIRGINIA BUREAU FOR PUBLIC HEALTH
OFFICE OF LABORATORY SERVICES

ENVIRONMENTAL CHEMISTRY
BIG CHIMNEY, WEST VIRGINIA
Updated 4/9/03



ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-79 Final Customer Report

Wayne Morganroth
Laboratory Supervisor
West Virginia Dept of Health
Environmental Chemistry
4710n Chimney Drive, Siute G
Charleston, WV 25302

EPA ID: WV00003
ERA Laboratory Code: W2134-01
Report Issued: 04/23/03

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Metals							
1000	Aluminum	µg/L	531.0	498	443 - 553	Acceptable	SM 3113 B
0140	Antimony †	µg/L	14.1	14.8	10.4 - 19.2	Acceptable	SM 3113 B
0001	Arsenic †	µg/L	107.0	106	92.8 - 118	Acceptable	SM 3113 B
0002	Barium †	µg/L	1050.0	1030	876 - 1180	Acceptable	EPA 200.7
0141	Beryllium †	µg/L	8.50	7.49	6.37 - 8.61	Acceptable	SM 3113 B
0226	Boron †	µg/L		747	697 - 822		
0003	Cadmium †	µg/L	22.6	23.1	18.5 - 27.7	Acceptable	SM 3113 B
0004	Chromium †	µg/L	42.9	44.3	37.7 - 50.9	Acceptable	SM 3113 B
0091	Copper †	µg/L	151.0	147	132 - 162	Acceptable	SM 3113 B
1070	Iron	µg/L	884.0	924	849 - 1000	Acceptable	SM 3111 B
0005	Lead †	µg/L	52.9	52.9	37.0 - 68.8	Acceptable	SM 3113 B
0236	Manganese †	µg/L	568.0	561	522 - 590	Acceptable	SM 3111 B
0237	Molybdenum †	µg/L		98.6	83.0 - 113		
0142	Nickel †	µg/L	84.8	87.7	74.5 - 101	Acceptable	SM 3113 B
0007	Selenium †	µg/L	77.5	73.1	58.5 - 87.7	Acceptable	SM 3113 B
1150	Silver	µg/L	256.0	248	224 - 272	Acceptable	SM 3113 B
0143	Thallium †	µg/L	7.31	7.27	5.09 - 9.45	Acceptable	EPA 200.9
1185	Vanadium	µg/L		762	711 - 811		
0239	Zinc †	µg/L	572.0	602	552 - 648	Acceptable	SM 3111 B
Mercury							
0006	Mercury †	µg/L	2.69	3.05	2.14 - 3.97	Acceptable	EPA 245.1
pH							
0026	pH †	S.U.	5.42	5.40	4.86 - 5.94	Acceptable	EPA 150.1
Inorganics							
1575	Chloride	mg/L	111	114	107 - 121	Acceptable	EPA 300.0
1610	Conductivity	µmhos/cm	534.0	575	544 - 606	Not Acceptable	SM 2510 B
0010	Fluoride †	mg/L	2.08	2.10	1.89 - 2.31	Acceptable	EPA 300.0
0009	Nitrate as N †	mg/L	3.50	3.52	3.17 - 3.87	Acceptable	EPA 353.2
1820	Nitrate + Nitrite as N	mg/L	3.50	3.52	3.17 - 3.87	Acceptable	EPA 353.2
1125	Potassium	mg/L		14.1	12.7 - 15.5		
0145	Sulfate †	mg/L	14.0	14.6	12.5 - 16.4	Acceptable	EPA 300.0
0024	Total Dissolved Solids at 180°C †	mg/L	383	381	245 - 517	Acceptable	SM 2540 C
Alkalinity & Sodium							
0027	Alkalinity (as CaCO3) †	mg/L	33.0	31.3	29.8 - 35.8	Acceptable	SM 2320 B

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01
† Indicates analytes included in ERA's NIST/NVLAP accreditation. Lab Code 200386-0

NVLAP® Lab code: 200386-0

Freedom_0006095_0174

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-79 Final Customer Report

Wayne Morganroth
Laboratory Supervisor
West Virginia Dept of Health
Environmental Chemistry
4710n Chimney Drive, Siute G
Charleston, WV 25302

EPA ID: WV00003
ERA Laboratory Code: W2134-01
Report Issued: 04/23/03

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Alkalinity & Sodium (Cont.)							
0029	Sodium †	mg/L	14.0	14.4	13.3 - 15.9	Acceptable	SM 3111 B
Turbidity							
0023	Turbidity †	NTU	3.29	3.34	2.91 - 4.04	Acceptable	EPA 180.1
Nitrite							
0092	Nitrite as N †	mg/L	0.81	0.811	0.689 - 0.933	Acceptable	EPA 353.2
Cyanide							
0146	Cyanide †	mg/L	0.20	0.227	0.170 - 0.284	Acceptable	SM 4500 CN F
Hardness							
1755	Total Hardness as CaCO3	mg/L	236.0	236	211 - 255	Acceptable	SM 2340 C
0025	Calcium Hardness as CaCO3 †	mg/L	206.0	209	196 - 223	Acceptable	SM 3500 Ca D
1035	Calcium	mg/L	82.6	83.8	76.5 - 93.4	Acceptable	SM 3500 Ca D
1085	Magnesium	mg/L	7.29	6.62	5.99 - 7.21	Not Acceptable	SM 3500 Mg E

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01
† Indicates analytes included in ERA's NIST/NVLAP accreditation. Lab Code 200386-0

NVLAP® Lab code: 200386-0

Freedom_0006095_0175

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-72 Final Complete Report

Wayne Morganroth
Laboratory Supervisor
West Virginia Dept of Health
Environmental Chemistry Lab
4710 Chimney Dr Ste G
Charleston, WV 25302

EPA ID: WV00003
ERA Laboratory Code: W2134-01
Report Issued: 09/20/02

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Metals							
1000	Aluminum	µg/L	300.0	293	257 - 331	Acceptable	SM 3113 B
0140	Antimony †	µg/L	23.3	20.1	14.1 - 26.1	Acceptable	SM 3113 B
0001	Arsenic †	µg/L	110.0	108	94.6 - 121	Acceptable	SM 3113 B
0002	Barium †	µg/L	1130.0	1090	927 - 1250	Acceptable	EPA 200.7
0141	Beryllium †	µg/L	6.19	6.35	5.40 - 7.30	Acceptable	SM 3113 B
0226	Boron †	µg/L		823	767 - 907		
0003	Cadmium †	µg/L	22.9	21.7	17.4 - 26.0	Acceptable	SM 3113 B
0004	Chromium †	µg/L	116.0	110	93.5 - 127	Acceptable	SM 3113 B
0091	Copper †	µg/L	851.0	818	736 - 900	Acceptable	SM 3113 B
1070	Iron	µg/L	121.0	124	111 - 139	Acceptable	SM 3111 B
0005	Lead †	µg/L	92.6	87.5	61.3 - 114	Acceptable	SM 3113 B
0236	Manganese †	µg/L	301.0	300	279 - 316	Acceptable	SM 3111 B
0237	Molybdenum †	µg/L		40.1	33.4 - 46.6		
0142	Nickel †	µg/L	193.0	189	161 - 217	Acceptable	SM 3113 B
0007	Selenium †	µg/L	51.7	52.7	42.2 - 63.2	Acceptable	SM 3113 B
1150	Silver	µg/L	319.0	324	293 - 356	Acceptable	SM 3113 B
0143	Thallium †	µg/L	4.19	4.05	2.84 - 5.27	Acceptable	EPA 200.9
1185	Vanadium	µg/L		324	301 - 344		
0239	Zinc †	µg/L	708.0	707	649 - 761	Acceptable	SM 3111 B
Mercury							
0006	Mercury †	µg/L	2.11	2.24	1.57 - 2.91	Acceptable	EPA 245.1
pH							
0026	pH †	S.U.	7.47	7.40	6.66 - 8.14	Acceptable	EPA 150.1
Inorganics							
1575	Chloride	mg/L	81.0	84.0	78.6 - 89.2	Acceptable	EPA 300.0
1610	Conductivity	µmhos/cm	541.0	535	506 - 564	Acceptable	SM 2510 B
0010	Fluoride †	mg/L	5.85	5.87	5.28 - 6.46	Acceptable	EPA 300.0
0009	Nitrate as N †	mg/L	4.45	4.67	4.20 - 5.14	Acceptable	EPA 353.2
1820	Nitrate + Nitrite as N	mg/L	4.45	4.67	4.20 - 5.14	Acceptable	EPA 353.2
1125	Potassium	mg/L		25.1	22.8 - 27.5		
0145	Sulfate †	mg/L	28.0	29.5	26.1 - 32.6	Acceptable	EPA 300.0
0024	Total Dissolved Solids at 180°C †	mg/L	361.0	359	232 - 486	Acceptable	SM 2540 C
Alkalinity & Sodium							
0027	Alkalinity (as CaCO3) †	mg/L	31.0	30.0	28.6 - 34.4	Acceptable	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01
† Indicates analytes included in ERA's NIST/NVLAP accreditation. Lab Code 200386-0

NVLAP® Lab code: 200386-0

Freedom_0006095_0176

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-72 Final Complete Report

Wayne Morganroth
Laboratory Supervisor
West Virginia Dept of Health
Environmental Chemistry Lab
4710 Chimney Dr Ste G
Charleston, WV 25302

EPA ID: WV00003
ERA Laboratory Code: W2134-01
Report Issued: 09/20/02

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Alkalinity & Sodium (Cont.)							
0029	Sodium †	mg/L	13.6	13.5	12.4 - 15.0	Acceptable	
Turbidity							
0023	Turbidity †	NTU	1.35	1.43	1.20 - 1.86	Acceptable	EPA 180.1
Nitrite							
0092	Nitrite as N †	mg/L	1.60	1.58	1.34 - 1.82	Acceptable	EPA 353.2
Cyanide							
0146	Cyanide †	mg/L	0.18	0.198	0.149 - 0.248	Acceptable	SM 4500 CN F
Hardness							
1755	Total Hardness as CaCO3	mg/L	283.0	281	239 - 323	Acceptable	SM 2340 C
0025	Calcium Hardness as CaCO3 †	mg/L	219.0	223	209 - 237	Acceptable	SM 3500 CaD
1035	Calcium	mg/L	87.8	89.2	81.6 - 99.2	Acceptable	SM 3500 CaD
1085	Magnesium	mg/L	15.6	14.3	12.9 - 15.5	Not Acceptable	SM 3500 Mg E

RECEIVED
SEP 26 2002

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01
† Indicates analytes included in ERA's NIST/NVLAP accreditation. Lab Code 200386-0

NVLAP® Lab code 200386-0

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ENVIRONMENTAL
RESOURCE ASSOCIATES®
The Industry Standard™

April 15, 2002

Charles Jones Jr.
EPA Region III
1650 Arch Street
Philadelphia, Pennsylvania 19103

FAX 215-814-2302

Dear Charles:

On April 10, 2002, West Virginia Department of Health located in Charleston, West Virginia, participated in ERA's QuiK™ Response Performance Evaluation Program. The following result was reported to ERA by West Virginia Department of Health for the PE standard, lot WV010. The Certified Value and the QuiK™ Response Acceptance Limits were not available to West Virginia Department of Health.

If you have any questions, please contact either myself, or Shawn Kassner, Proficiency Testing Program Manager, at 1-800-372-0122.

Sincerely,

Anne E. Rager
QuiK™Response Coordinator

Cc: Project File Number WV010

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ENVIRONMENTAL RESOURCE ASSOCIATES®
The Industry Standard™

QuiK™ Response PE Standards
State of West Virginia

Final Report

PotableWatR™ Metals

Customer: West Virginia Dept of Health
Lot Number: WV010
State ID Number: WV00003/00003 C
Method: SM 3113 B

Parameter	Units	Reported Value	Certified Value	QuiK™ Response Limits	Comment
arsenic	µg/l	71.0	69.4	60.7 - 77.5	Acceptable

Results reported by: Wayne Morganroth - West Virginia Dept of Health

Date of Report: 4/15/02

ENVIRONMENTAL
RESOURCE ASSOCIATES®
The Industry Standard™

December 14, 2001

Charles Jones Jr.
Bureau of Public Health
Mail Code 3ES10
1650 Arch Street
Philadelphia, PA 19103-2029

FAX 215-814-2783

Dear Charles:

On November 29, 2001, Bureau of Public Health located in Charleston, West Virgina, participated in ERA's QuiK™ Response Performance Evaluation Program. The following result was reported to ERA by Bureau of Public Health for the PE standard, lot 11290101. The Certified Value and the QuiK™ Response Acceptance Limits were not available to Bureau of Public Health.

If you have any questions, please contact either myself, or Shawn Kassner, Proficiency Testing Program Manager, at 1-800-372-0122.

Sincerely,

Anne E. Rager
QuiK™Response Coordinator

Cc: Project File Number 11290101

ENVIRONMENTAL RESOURCE ASSOCIATES®
The Industry Standard™

QuiK™ Response PE Standards

Final Report

PotableWatR™ Metals

Customer: Bureau of Public Health
Lot Number: 11290101
State ID Number: WV00003
Method: SM3113B

Parameter	Units	Reported Value	Certified Value	QuiK™ Response Limits	Comment
arsenic	µg/l	118.0	105	91.9 - 117	Not Acceptable

Results reported by: Wayne Morganroth - Bureau of Public Health

Date of Report: 12/14/01

TOTAL P.03

Corrective Action Plan for Failed Arsenic PT WS – 58

Facts: - Arsenic Calibration Standards were prepared day before analysis of PT

- Selenium was analyzed from same dilution of PT stock as Arsenic and recovered within limits

- Arsenic QCs recovered at 106.0% of True Value (T.V).

- Initial Instrument Performance Check (mid-range standard) recovered 103.7%, subsequent checks recovered at 107.1%, 109.6%, and 106.5%: attendant QC Blanks all recovered below IDL (Instrument Detection Limit).

- RPDs between Lab Duplicates were acceptable

- Superlamp boost that day was 26 mA (which is very high) producing PMV of 404.6 which is also high

Conclusion: While initial and subsequent QC were acceptable there was some evidence of positive instrumental drift. We are proposing that this was due to the age of the superlamp which has been in use since March 2000. Arsenic superlamps have not had a good history of longevity and signal stability is heavily dependent on the performance of the lamp which deteriorates after about a year of use. A new Arsenic superlamp has been ordered for use on a "make-up" PT sample

Supervisor's Comment: Added August 22, 2001:

The Arsenic superlamp has been on order for nearly one month (order initiated on July 26, 2001), and has not been received as of this date. As a consequence the order for the Arsenic "make-up" PT sample will not be placed until both: 1. Larry has returned from the EPA Laboratory Directors and SDWA Certification Officers Meeting in Ft. Meade, MD next week, and 2. The Arsenic superlamp has been received. This will prevent having the make-up PT sample in-house, potentially for quite some time (while "eating up" the time allotted by the PT provider for analysis and return of results), before receipt of the superlamp and Larry is able to block out some time to perform the requisite analyses.

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-58 Final Complete Report

BUREAU OF PUBLIC HEALTH, OLS
Environmental Chemistry Lab
4710 Chimney Dr Ste G
Charleston, Wv 25302

EPA ID: WV00003 **Report Issued: 07/19/01**
State ID: 0003C
ERA Laboratory Code: W2134-01

ERA Standard/Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Metals						
Aluminum	µg/l	2990.0	3000	2720 - 3260	Acceptable	SM 3113 B
Antimony	µg/l	33.2	35.6	24.9 - 46.3	Acceptable	SM 3113 B
Arsenic	µg/l	103.0	90.8	79.5 - 101	Not Acceptable	SM 3113 B
Barium	µg/l	911.0	910	774 - 1050	Acceptable	EPA 200.7
Beryllium	µg/l	7.27	6.34	5.39 - 7.29	Acceptable	SM 3113 B
Boron	µg/l		804	750 - 886		
Cadmium	µg/l	29.4	28.4	22.7 - 34.1	Acceptable	SM 3113 B
Chromium	µg/l	140.0	135	115 - 155	Acceptable	SM 3113 B
Copper	µg/l	1680.0	1620	1460 - 1780	Acceptable	SM 3113 B
Iron	µg/l	1560.0	1560	1440 - 1690	Acceptable	SM 3111 B
Lead	µg/l	95.8	86.1	60.3 - 112	Acceptable	SM 3113 B
Manganese	µg/l	323.0	321	298 - 338	Acceptable	SM 3113 B
Molybdenum	µg/l		87.7	73.8 - 101		
Nickel	µg/l	338.0	354	301 - 407	Acceptable	SM 3113 B
Selenium	µg/l	78.2	75.3	60.2 - 90.4	Acceptable	SM 3113 B
Silver	µg/l		256	232 - 281		
Thallium	µg/l	5.46	5.01	3.51 - 6.51	Acceptable	EPA 200.9
Vanadium	µg/l		790	737 - 841		
Zinc	µg/l	1650.0	1640	1510 - 1760	Acceptable	SM 3111 B
Mercury						
Mercury	µg/l	3.20	3.38	2.37 - 4.39	Acceptable	EPA 245.1
pH						
pH	S.U.	8.41	8.37	7.53 - 9.21	Acceptable	EPA 150.1
Inorganics						
Chloride	mg/l	111	112	105 - 119	Acceptable	EPA 300.0
Conductivity	µmhos	625	616	583 - 649	Acceptable	SM 2510B
Fluoride	mg/l	1.65	1.74	1.57 - 1.91	Acceptable	EPA 300.0
Nitrate as N	mg/l	5.90	5.93	5.34 - 6.52	Acceptable	EPA 353.2
Potassium	mg/l		20.1	18.2 - 22.1		
Sulfate	mg/l	21.0	22.0	19.2 - 24.5	Acceptable	EPA 300.0
Total dissolved solids	mg/l	398	408	262 - 554	Acceptable	SM 2540C
Alkalinity & Sodium						
Alkalinity (as CaCO3)	mg/l	46.0	45.5	43.2 - 51.0	Acceptable	SM 2320B
Sodium	mg/l	20.7	20.7	19.2 - 22.8	Acceptable	SM 3111 B
Turbidity						
Turbidity	NTU	1.40	1.59	1.34 - 2.04	Acceptable	EPA 180.1
Nitrite						
Nitrite as N	mg/l	1.33	1.32	1.12 - 1.52	Acceptable	EPA 353.2
Hardness						
Total Hardness as CaCO3	mg/l	198	196	167 - 225	Acceptable	SM 2340C
Calcium Hardness as CaCO3	mg/l	146	149	140 - 160	Acceptable	SM 3500CaD

NVLAP® Lab code: 200386-0

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BUREAU OF PUBLIC HEALTH, OLS
Environmental Chemistry Lab
4710 Chimney Dr Ste G
Charleston, Wv 25302

EPA ID: WV00003 **Report Issued: 07/19/01**
State ID: 0003C
ERA Laboratory Code: W2134-01

ERA Standard/Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Hardness (Cont.)						
Calcium	mg/l	58.5	59.6	53.8 - 67.0	Acceptable	SM 3500CaD
Magnesium	mg/l	12.6	11.6	10.5 - 12.6	Acceptable	SM 2340C

NVLAP Lab code 200384-0

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ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-52 Final Customer Report

ERA Laboratory Code: W2144-01 **EPA ID: WV00003** **State ID:** **Report Issued: 01/19/01**

ERA Standard	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Metals	Aluminum	µg/l	1080.0	954	858 - 1050	Not Acceptable	SM 3113 B
	Antimony	µg/l	25.0	24.6	17.2 - 32.0	Acceptable	SM 3113 B
	Arsenic	µg/l	53.7	49.3	43.1 - 55.1	Acceptable	SM 3113 B
	Barium	µg/l	634.0	626	532 - 720	Acceptable	EPA 200.7
	Beryllium	µg/l	7.93	7.14	6.07 - 8.21	Acceptable	SM 3113 B
	Boron	µg/l		611	573 - 670		
	Cadmium	µg/l	32.6	31.2	25.0 - 37.4	Acceptable	SM 3113 B
	Chromium	µg/l	146.0	160	136 - 184	Acceptable	SM 3113 B
	Copper	µg/l	1600.0	1640	1480 - 1800	Acceptable	SM 3113 B
	Iron	µg/l	90.0	85.1	75.6 - 96.9	Acceptable	SM 3111 B
	Lead	µg/l	20.2	20.0	14.0 - 26.0	Acceptable	SM 3113 B
	Manganese	µg/l	43.5	37.9	33.7 - 40.7	Not Acceptable	SM 3111 B
	Molybdenum	µg/l		126	106 - 145		
	Nickel	µg/l	345.0	387	329 - 445	Acceptable	SM 3113 B
	Selenium	µg/l	35.6	35.7	28.6 - 42.8	Acceptable	SM 3113 B
	Silver	µg/l		83.0	74.7 - 91.2		
	Thallium	µg/l	5.64	5.43	3.80 - 7.06	Acceptable	EPA 200.9
	Vanadium	µg/l		706	658 - 752		
	Zinc	µg/l	1180.0	1140	1050 - 1220	Acceptable	SM 3111 B
Mercury	Mercury	µg/l	6.16	7.22	5.05 - 9.39	Acceptable	EPA 245.1

NVLAP®
Lab code 200385-0

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-52 Final Customer Report

ERA Laboratory Code: W2144-01 EPA ID: WV00003 State ID: Report Issued: 01/19/01

ERA Standard	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
pH	pH	S.U.	8.97	8.90	8.01 - 9.79	Acceptable	EPA 150.1
Inorganics	Chloride	mg/l	88.0	89.2	83.6 - 94.7	Acceptable	EPA 300.0
	Conductivity	µmhos	548	533	504 - 562	Acceptable	SM 2510B
	Fluoride	mg/l	2.55	2.60	2.34 - 2.86	Acceptable	SM 4500-FC
	Nitrate as N	mg/l	5.74	5.98	5.38 - 6.58	Acceptable	EPA 353.2
	Potassium	mg/l		22.1	20.0 - 24.2		
	Sulfate	mg/l	8.00	8.79	7.21 - 10.0	Acceptable	EPA 300.0
	Total dissolved solids	mg/l	376	376	242 - 510	Acceptable	SM 2540 C
Alkalinity & Sodium	Alkalinity (as CaCO3)	mg/l	39.0	38.6	36.7 - 43.6	Acceptable	SM 2320 A
	Sodium	mg/l	17.8	17.8	16.5 - 19.6	Acceptable	SM 3111 B
Turbidity	Turbidity	NTU	4.44	5.12	4.50 - 6.08	Not Acceptable	EPA 180.1
Residual Chlorine	Free residual chlorine	mg/l		1.10	0.887 - 1.31		
	Total residual chlorine	mg/l		1.29	0.968 - 1.61		
Nitrite	Nitrite as N	mg/l	1.65	1.66	1.41 - 1.91	Acceptable	EPA 353.2
Nutrients	ortho-Phosphate as P	mg/l		1.09	1.01 - 1.15		
Cyanide	Cyanide	mg/l		0.180	0.135 - 0.225		
TOC	Total organic carbon	mg/l		3.90	3.51 - 4.49		
Chlorite	Chlorite	µg/l		251	174 - 370		
Bromate & Chlorate	Bromate	µg/l		14.6	3.08 - 28.7		
	Chlorate	µg/l		127	104 - 146		
Bromide	Bromide	µg/l		178	151 - 208		
Hardness	Total Hardness as CaCO3	mg/l	176	175	149 - 201	Acceptable	SM 2340 C
	Calcium Hardness as CaCO3	mg/l	148	155	145 - 166	Acceptable	SM 3500 CA D
	Calcium	mg/l	59.3	62.2	56.2 - 69.8	Acceptable	SM 3500 CA D
	Magnesium	mg/l	6.80	4.88	4.42 - 5.33	Not Acceptable	SM 2340 C
Heterotrophic Plate Ct	Heterotrophic Plate Count	CFU/ml		53	36 - 66		

NVLAP®
Lab code: 200386-0

ENVIRONMENTAL RESOURCE ASSOCIATES®

WS-52 Final Customer Report

ERA Laboratory Code: W2144-01 **EPA ID: WV00003** **State ID:** **Report Issued: 01/19/01**

ERA Standard	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
pH	pH	S.U.		8.90	8.01 - 9.79		
Inorganics	Chloride	mg/l		89.2	83.6 - 94.7		
	Conductivity	µmhos		533	504 - 562		
	Fluoride	mg/l	2.72	2.60	2.34 - 2.86	Acceptable	EPA 300.0
	Nitrate as N	mg/l		5.98	5.38 - 6.58		
	Potassium	mg/l		22.1	20.0 - 24.2		
	Sulfate	mg/l		8.79	7.21 - 10.0		
	Total dissolved solids	mg/l		376	242 - 510		
Alkalinity & Sodium	Alkalinity (as CaCO3)	mg/l		38.6	36.7 - 43.6		
	Sodium	mg/l		17.8	16.5 - 19.6		
Turbidity	Turbidity	NTU		5.12	4.50 - 6.08		
Residual Chlorine	Free residual chlorine	mg/l		1.10	0.887 - 1.31		
	Total residual chlorine	mg/l		1.29	0.968 - 1.61		
Nitrite	Nitrite as N	mg/l		1.66	1.41 - 1.91		
Nutrients	ortho-Phosphate as P	mg/l		1.09	1.01 - 1.15		
Cyanide	Cyanide	mg/l		0.180	0.135 - 0.225		
TOC	Total organic carbon	mg/l		3.90	3.51 - 4.49		
Chlorite	Chlorite	µg/l		251	174 - 370		
Bromate & Chlorate	Bromate	µg/l		14.6	3.08 - 28.7		
	Chlorate	µg/l		127	104 - 146		
Bromide	Bromide	µg/l		178	151 - 208		
Hardness	Total Hardness as CaCO3	mg/l		175	149 - 201		
	Calcium Hardness as CaCO3	mg/l		155	145 - 166		
	Calcium	mg/l		62.2	56.2 - 69.8		
	Magnesium	mg/l		4.88	4.42 - 5.33		
Heterotrophic Plate Ct	Heterotrophic Plate Count	CFU/ml		53	36 - 66		

NVLAP® Lab code 200388-0

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Evaluation of State Laboratory Certification Programs:

From: Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures, Quality Assurance, EPA 815-B-97-001 United States Office of Ground Water and Drinking Water Environmental Protection Agency, Cincinnati, OH 45268, March 1997

EPA Regions:

* The Regions oversee the certification programs in the States. The Regions' responsibilities are:

- Perform an annual review of State certification programs and performance evaluation results and monitor the adequacy of State programs for certifying laboratories, as described in Chapter III [***R3 uses annual questionnaires. Does on-site review every three years];***

* "...this manual (Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures, Quality Assurance) must be the basis for the on-site audits, conducted by EPA, of principal State laboratories, laboratories on Federal Indian lands, and drinking water laboratories in non-primacy States."

Primacy States

* Primacy States are required to establish and maintain a State program for the certification of laboratories conducting analyses of drinking water compliance samples, unless all compliance samples are analyzed in the State laboratory.

* The States must designate a certification officer or officers, certified by the EPA administrator or his or her designee as the person responsible for the certification program.

* States are responsible for the certification of the public and private laboratories in their State.

* This includes auditing the laboratories and reviewing the PE data.

* States should also provide technical assistance to laboratories.

* They may also choose to certify laboratories outside their State either by an on-site evaluation or reciprocity.

Chapter III Implementation

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Evaluation of Certification Programs:

* The Regions and OGWDW should monitor the certification programs under their purview annually. ***R3 uses annual questionnaires. Does on-site review every three years.***

* The adequacy of programs for certifying laboratories is evaluated by assessing each program's:

    * scope;

    * staffing;

    * resources;

    * policy;

    * procedures; and

    * effectiveness.

"This should be done in person during an on-site audit when possible and at least by means of a questionnaire in the other years.

* The adequacy of these essential program elements is evaluated by:

    * Reviewing the program's plan;

    * responsibilities;

    * organizational structure;

    * staff (including educational background and experience);

    * scope and description of the certification process, downgrading criteria and processes;

    * and use of PE samples;

    * Requesting an annual program report that includes program highlights, training, continuing education efforts, number of on-site evaluations performed, listing of laboratories certified by discipline or contaminant, and any certification downgrading or upgrading actions along with reasons for those actions ***Region 3 has this as part of the Regional Questionnaire***;

    * Observing on-site audits of drinking water laboratories to allow EPA Regional

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certification officers to evaluate specific elements of the State certification program;

* Encouraging State and Regional laboratory auditors to observe on-site audits of their own and other laboratories as on-the-job training; ***Region 3 has this as part of the On-site of State Laboratories***

* Sponsoring annual meetings of certification officers to discuss program issues, policies, and problems. Key Regional, NERL, and OGWDW and State personnel should be invited to participate.

Additional Items (Region 3):

* Example inspection reports.

* Training of Cos/records (do they get on-the-job training, NELAC says min. of four). DO COs GET SAFETY TRAINING (REQUIRED OF EPA ASSESSORS)?

* Filing system for reports/tracking of corrective actions, etc.

* System for tracking of PT performance.

* Use of PTs and PT requirements (method and analyte)

* PT schedule (Lab's option or set by State)?

* Outreach/training provided to regulated community

* Written procedures/policies or program description.

* "Data Audit" of files including examples of certificates and correspondences–especially reports/time lines and corrective actions.

* What is the emphasis of the State's on-site review (encourage review of data a part of on-site assessments).

* Time State spends on site and number of auditors?

* Do they have the resources to do the job?

* Encourage the use of method specific analytical checklists (microbiology checklists is required).

* Lab Ids?

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* Certification groups?

* Inspection schedule:
  Are they able to get on-site every three years?

  How long for reports to be sent to the lab?

  Do they have a projected schedule for on-sites?

* Does State require a minimum number of samples to be analyzed by SDWA protocols for a lab to be in their program (assures lab is practices/experienced and that there is data to review)?

* Is Certification by method and Analyte?

* Do they have a good pre-survey package?

* Pick 3-4 lab files at random and check:
  Final Reports;
  PT results;
  Corrective Action Reports;
  Certificates .

Freedom_0006095_0198

Regional SDWA Laboratory Certification
Review Questionnaire:

Date: May 30, 2003

Completed by: Wayne Morganroth Title: Laboratory Supervisor, Chemistry CO

Telephone: 1-304-558-0197 Fax: 1-304-559-4143

Email: waynemorganroth@wvdhhr.org

Organization: WV Bureau of Public Heaalth, O. L. S., Environmental Chemistry Laboratory
4710 Chimney Drive, Suite G, Charleston, WV 25302.

1. Provide a listing of all Microbiology laboratories your State Certifies and the date of the last on-site inspection and the projected date for the next on-site inspection.

Does not apply to our laboratory.

2. Provide a listing of all Chemistry laboratories your state certifies and the date of the last on-site inspection and the projected date for the next on-site inspection.

Laboratory Name	**In-State/Out of State**	**Date Last On-Site**	**Proj. Date Next On-S.**
A C & S	In-State	July 30, 2002	June 2005
Analabs, Inc.	In-State	July 19, 2001	May 2004
C T & E, Env. Svcs.	In-State	August 19, 1997	August 2003
REI Consultants	In-State	October 17, 1997	July 2003
Reliance Laboratories	In-State	October 15, 1997	September 2003
WV-American Water	In-State	June 28, 2001	June 2004
Special analytical Svcs	In-State	August 8, 2001	August 2004
Wheeling Water Trtmt.	In-State	September 26, 2001	September 2004
Am Water Works	Out-of-State	* NA Do not perform out-of State On-sites	
Laboratory Name	**In-State/Out -of-State**	**Date Last On-Site**	**Proj Date Next On-St**
Aqua Tech Env Labs - Inorganic Testing	Out-of-State	* NA	
Aqua Tech Env Labs - Organic Testing	Out-of-State	* NA	
Env Eng & Tech.	Out-of-State	* NA	
Env Health Labs	Out-of-State	* NA	

Lancaster Labs	Out-of-State	* NA	
MWH Laboratories	Out-of-State	* NA	
National Testing	Out-of-State	* NA	
STL W. Sacramento	Out-of-State	* NA	
Test America	Out-of-State	* NA	
Triangle Laboratories	Out-of-State	* NA	
US Army Ctr for Health P & Pr Med.	Out-of-State	* NA	

3. Provide a listing of all Rad Chemistry Laboratories your State certifies and the date of the last on-site inspection and the projected date for the next on-site inspection.

Our certification staff does not certify Rad Chemistry Laboratories. Certification of these labs is performed by the Radiological Section of the Office of Environmental Health Service.

4. Soes your State have the resources to carry out the certification program properly (on-sites, PT tracking, certification tracking, issuance of certificates)? What are the major bottlenecks/problems/shortfalls?

No. Our certification program suffers most from a lack of certification personnel. We now have two fully certified (inorganic and organic parameters) COs. However, both have a host of other responsibilities so it is very difficult to block out time for on-site inspections and the writing of the follow-up reports. Scheduling of on-sites is additionally complicated by the fact that we have only one State automobile at our disposal which must be shared with any employee of OLS (with a total of 50 to 60 employees) that may need the car for travel. I guess our greatest complaint is where do you get the necessary time: for preparing for the on-site, time to actually perform the on-site and then time to do a good job in writing the inspection report.

5. EPA requires laboratories to pass a PT for each contaminant by each method, each year for which they are seeking certification. Who in your State keeps the PT data for the private laboratories?

The PT data is maintained by Wayne Morganroth, the laboratory supervisor.

Are they checking to be sure the private laboratories pass a PT for contaminants by each method each year for which they are seeking certification?

Yes.

How does your State track the PT performance of Laboratories?

Presently it is being done through the use of a fill-in form that is completed by hand.

Is there an electronic database?

No.

6. Do you have comments, good or bad, about the new privatized PT program?

In general the program seems to work rather well. My main complaint is that certification record keeping has been complicated - different PT providers use different arrangements of data making it more difficult to arrange in each certified

laboratory's file. There also doesn't seem a consistent categorization of some analytes. Is a particular organic a pesticide, a herbicide or listed as an SOC?

Are the providers including all the necessary information on their reports to you?

For the most part, yes. I think that all sheets making up the PT report should be clearly labeled with the name of the laboratory submitting PT results. They should also include the date of the PT study - such as starting and ending dates. In the past I have seen a report or two from one provider (whose name escapes now) that had no date at all on the results sheets - if these sheets become separated from any accompanying descriptive letter it becomes impossible to know to what year it should be credited..

7. Where does your State get their PT samples?

Environmental Resource Associates.

Is the State satisfied with them?

Quite satisfied.

8. What schedule does your State follow for PTs, e.g., specified time of year for studies and make-up studies?

During the first three months of each calendar year laboratories must analyze WS PT samples for all parameters (by all methods used in analyzing for each parameter) for which they hold, or are seeking, certification. If a laboratory fails to demonstrate satisfactory performance for all PT parameters during that period the laboratory must acceptably analyze all "missed" parameters by September 30 of that year - by all methods for which they wished to be certified .

9. List your State's SDWA Certification Officers and their education and related experience.

Wayne Morganroth, Ph.D. in Chemistry. Successfully attended certification courses in inorganic and organic parameters given by EPA at Cincinnati, OH. Have participated in certification work since approximately 1995.

Larry Duffield, BS in Biology. Has passed both the inorganic and organic certification courses given by EPA at Cincinnati, OH. He has been involved in the certification effort since 1990 and possibly a few years before that date.

10. List training provided to SDWA Certification Officers in the last year.

Larry Duffield successfully attended the EPA Certification Course for Organic Parameters in June of 2002.

11. List training provided by State to SDWA certification community in the last year?

None.

12. Provide an organizational structure of the State's Lab Certification Program and indicate to what program element/s it reports.

O. L. S. Director, Dr Andrea Labik

Associate Director, Charlotte Billingsley

Certification Officers, Wayne Morganroth & Larry Duffield

In-program reporting is made to both the Director and Associate Director of O. L. S. Keep them informed about certification activity, WS PT results and any communications with EPA offices.

13. Provide a description of the certification procedures including downgrading criteria and process (Note: if your State follows the Lab Cert Manual, indicated revision and section/page number)

Our certification program using the certification procedures, including downgrading and process that are given in EPA *Manual for the Certification of Laboratories Analyzing Drinking Water*, Fourth Edition, March 1997 in Chapter III, pages 1 through 9.

Please indicate if you have written Quality Manuals/SOPs for your lab certification program and provide their titles.

We have these documents on hand. The Titles are:

Quality Manual: WV DHHR Office of Laboratory Services
Manual of Quality Assurance, Environmental Chemistry Laboratory

Certification SOP: Office of Laboratory Services, Environmental Chemistry
Standard Operating Procedures, EPA/SDWA Laboratory
Certification

14. List any certification downgrading or upgrading actions in the last year with reason for those actions.

During 2002 Sturm Environmental Services supplied very little WS PT data. As a mean of giving them the benefit of my doubt their Director was called and a request made for all of the PT data for all of 2002. We were assured that the requisite data would be assembled and forwarded to our office within a matter of a few days. A month or two later we still had not received any PT results. At the time we were processing requests for annual certification renewals; since we had no way to assess the on-going competency the laboratory was decertified. Note: We have since learned that the laboratory director, who also was the QA/QC Officer no longer works for Sturm. The new QA/QC officer has notified me by phone that a search has been made for the PT data for 2002 and none could be found!
The laboratory has been notified of their decertification status; further, if they wish to be re-certified, they will be treated in the same manner as any new laboratory seeking certification.

The 2002 on-site examination of A. C. & S., was their first-hand evaluation. Prior to the on-site the laboratory had an interim certification - this status was given because I was acquainted with the laboratory and knew they had proper instrumentation and capable analysts. Since the on-site evaluation was excellent their status for all interim certified analytes was up-graded to fully certified.

15. List topics you would like on the next Region 3 SDWA CO's Meeting Agenda or for the national LabCert bulletin.

At t
he present time I am coming up empty here.

16. Provide example inspection reports for the last year, i.e., chemistry report.

Last year only one on-site investigation was performed. I performed the on-site. In order to give you more complete picture of how we conduct and report laboratory on-sites I am including the report of an on-site evaluation that was performed by Larry Duffield in July 2001.

17. Provide example corrective action reports from labs (correspond to report/s in #16).

Since I found no deviations for the on-site I conducted last year (A. C. & S., Inc.,) there was no need for a corrective action report.
The on-site investigation Larry Duffield conducted in July 2001 resulted in the de-certification of the laboratory. Since that time we have received no communication from the laboratory indicating an interest in seeking re-certification.

18. Provide example SDWA certificates or updates to certificates issued (correspond to report/s in #16).

Certificate and certified parameter sheet will be sent by separate mail since I do not have that information on disk.

19. Does your program approve laboratories for TOC and Specific Ultraviolet Absorption (SUVA)?

Yes

Are these formal approvals or does the program accept data from any laboratory submitting it?

We accept data from laboratories that have acceptable results for TOC and SUVA **Pts.**

20. Does your program certify laboratories for haloacetic acids (HAA), bromate, and chlorite analyses?

We certify only for HAA5s only.

21. How does your program handle the oversight of orthophosphate, alkalinity, calcium, silica, pH, conductivity.

I am not sure I understand the question, but I will try to answer. We presently have no demonstrated analytical capability for orthophosphate or silica. We could conceivably develope capability for silica, but the equipment we have for analyzing for orthophosphate is so old and questionable (in-so-far as reliable results) I don't think we could analyze for it - reliably that is. As a consequence if it is called for we could certify (or approve for use) methodologies for pH, conductivity, calcium and alkalinity.

STATE OF WEST VIRGINIA
DEPARTMENT OF HEALTH AND HUMAN RESOURCES

Bob Wise
Governor

ENVIRONMENTAL MICROBIOLOGY

Paul L. Nusbaum
Secretary

December 26, 2002

To: WV Drinking Water Laboratories Certified for Microbiology

From: Thomas L. Ong, Microbiologist Supervisor
Laboratory Certification Officer

RE: Laboratory Certification Information

I. Proficiency Testing

Beginning January 2003, all Proficiency Tests must be completed within the first three months of the year (January, February or March) and reported to this office by May 30 of each year. Any Repeat Studies (if necessary) must be done and reported to this office by September 30. Any laboratories that have not submitted a successful P.T. Study by September 30 will receive a certified letter with the intent to remove certification. Any laboratory that has Unacceptable Results on a P.T. Study must notify this office within 30 days of being notified of the Unacceptable Result and include a written Corrective Action Plan to include documentation of participation or intent to participate in another P.T. Study. Failure to submit a written Corrective Action Plan within the specified time frame will result in a certified letter with the intent to remove certification. The U.S.E.P.A. is recommending that P.T. Studies be treated like routine samples (i.e., logged into the laboratory system). A new report form (2 copies enclosed) is provided to simplify the reporting process. Instructions for completing the form are listed on the back and it must be completed and received by this office by May 30 of each year. This form will supply additional information that the P.T. Study Providers normally do not include on their reports. For example: when the study was received by the laboratory, when it was actually analyzed and who performed the analysis.

II. Laboratories Certified for Only Chromogenic/Fluorogenic Substrate Tests (Colilert, Colisure and E*colite)

There have been some recent discussions on the amount of Quality Control (QC) Records Required for the Chromogenic/Fluorogenic Substrate Tests. In the past, those items that were indirectly used in the testing process were generally not reviewed during on-site evaluations. However, it is the opinion of the U.S.E.P.A. that all items that are both indirectly and directly

BUREAU FOR PUBLIC HEALTH
OFFICE OF LABORATORY SERVICES
167 11th Avenue
South Charleston, WV 25303-1137

Phone: (304) 558-3530 FAX: (304) 558-2006

used meet all of the requirements listed in Chapter V of the *Manual for the Certifications of Laboratories Analyzing Drinking Water*, 4th Edition, March 1997. This all hinges on one item – Tryptic Soy Broth (TSB). This media (or some other non-selective broth) is required to verify sterility of the sample/test vessels and is therefore indirectly used in the chromogenic/fluorogenic substrate tests.

With regards to TSB, laboratories have two options: 1. Prepare the media in-house, or 2. Buy the media commercially prepared. Those laboratories that choose Option #1, preparing the media in-house, will have to meet all of the QC items with regards to the production of media: pH Meter (Item 3.1), Balance Records (Item 3.2), Autoclave Records (Item 3.5), Conductivity Meter (Item 3.8), Glassware and Plasticware (Item 3.16), Sterilization Procedures (Item 4.1), Reagent Grade Water (Item 4.3), Glassware Washing (Item 4.5) and Media (Item 5.1.7). Those laboratories that choose Option #2, buy the media commercially prepared, will only have to perform the QC listed in pH Meter (Item 3.1) and Media (Item 5.1.7). Regardless of whether this media is laboratory prepared or bought commercially, it must be checked before use with positive and negative controls, each lot for commercially prepared or each batch for laboratory prepared. This item is generally overlooked with respect to TSB due to the fact that it has an indirect relationship to the testing procedures. These items will all be looked at during up-coming on-site evaluations.

III. Reporting of Compliance Samples

The Office of Environmental Health Services – Environmental Engineering Division (OEHS-EED) has requested that Certified Drinking Water Laboratories report test results directly to them as they are responsible for enforcing the State Drinking Water Program. To bring about uniformity in the program, the Engineering Division has revised Form EW-112 to become the official method of reporting compliance data to the state. (An example of Form EW-112, Rev. 8/02 is enclosed; however, the form enclosed in not properly formatted. Please contact OEHS-EED for an official copy.) Several certified laboratories are already using forms similar to the EW-112 to report compliance data to the state. These forms are to be completed monthly for each Public Water System (one EW-112 per Public Water System) and received at the following address within 10 days after the end of the month:

Office of Environmental Health Services
Environmental Engineering Division
815 Quarrier Street, Suite 418
Charleston, WV 25301

ATTN: RD&C Unit

Once this system is operational, no other forms will be accepted for reporting compliance data. Laboratories must begin using this form beginning January 1, 2003 with the first reports to be received at the above address by the close of business February 10, 2003. For example, a public water supply collects samples on January 3, January 13 and January 23. These can all be combined onto one EW-112 (provided they are from the same system) and submitted to the RD&C Unit by the end of business, February 10, 2003.

The requirements for the reporting of positive total coliform samples and positive fecal coliform/*E. coli* samples has not changed. These must be reported (faxed) to the RD&C Unit at: (304) 558-0139 within 24 hours of completion of the laboratory test. If a phone call is necessary, laboratories may contact either Helen Crum (304) 558-6777 or David Stewart (304) 558-6742 who are compliance officers. Although these do not have to be faxed to the RD&C Unit on the EW-112, they may be faxed on the laboratories routine report form, they do have to be included on the EW-112 that is submitted for that particular system at the end of the month.

The Manual for the Certification of Laboratories Analyzing Drinking Water, 4th Edition, March 1997, lists in Chapter III under **Criteria and Procedures for Downgrading/ Revoking Certification Status** the following statement as reason for downgrading (or removing) certification:

"Failure to report compliance data to the public water system or the State drinking water program in a timely manner, thereby preventing compliance with Federal or State regulations and endangering public health. Data which may cause the system to exceed an MCL should be reported as soon as possible."

With the institution of any new procedure, there is always an implementation period in which issues will arise that need to be resolved. Please contact this office immediately with any problems or questions regarding this new system so that any problems may be resolved in a timely manner.

IV. Manual for the Certification of Laboratories Analyzing Drinking Water

The EPA's Manual for the Certification of Laboratories Analyzing Drinking Water, 4th Edition, March 1997 is currently undergoing another revision. This manual, referenced in State code, lists the requirements for laboratory certification. The 5th Edition is tentatively scheduled to be out by the end of this year (December 2002) and should be available on the EPA's web site. Once this manual is finalized a summary of the changes will be forwarded. Once the manual is released, laboratories should begin instituting the changes.

V. Contacts

The Office of Laboratory Services has recently received a new telephone system. Any questions regarding laboratory certification should be directed to the following:

Thomas L. Ong (304) 558-3530, Ext. 2710 e-mail: tomong@wvdhhr.org

E-mail is the preferred method of communication as it results in written documentation.

State Of West Virginia

Department of Health and Human Resources
Bureau For Public Health

Office of Laboratory Services

Certifies That

REI Consultants, Inc.

225 Industrial Park Road
Beaver, WV 25813

having duly met the requirements of the
Certification of Laboratories to Conducts Drinking Water Test
(64CSR 3-13)
is hereby approved as a

State Certified Drinking Water Laboratory

To perform the analyses indicated on the
Certified Parameter List
which must accompany this certificate

00412.CM
Certificate Number

Laboratory Director

January 01, 2003
Date of Issue

Certification Officer(s)

Certificate Expires on **December 31, 2003**

West Virginia Department of Health and Human Resources

Bureau For Public Health
Office of Laboratory Services

This is to certify that the following laboratory has been approved to perform the indicated procedures on drinking water in accordance with West Virginia 64CSR 3-13:

REI Consultants, Inc.
00412 CM
225 Industrial Park Road
Beaver, WV 25813

Issue Date: 1/1/2003 **LabDirector:** Claude Scott **Expiration Date:** 12/31/2003

Group: *Microbiology*			
Total Coliforms	SM9222B, SM9223B	Certified	Membrane Filter, Colilert
Fecal Coliforms/E. Coli	SM9221E, SM9223B	Certified	EC Medium, Colilert
Heterotrophic Bacteria	SM9215B	Certified	HPC - Pour Plate Method
Group: *Trace Metals Group I*			
Copper	200.8	Certified	
Lead	200.8	Certified	
Group: *Trace Metals Group II*			
Antimony	200.8	Certified	
Arsenic	200.8	Certified	
Barium	200.8	Certified	
Beryllium	200.8	Certified	
Cadmium	200.8	Certified	
Chromium	200.8	Certified	
Mercury	245.2	Certified	
Selenium	200.8	Certified	
Thallium	200.8	Certified	
Group: *Inorganicls Group I*			
Nitrate-N	300.0	Certified	

Freedom_0006095_0208

REI Consultants, Inc.

00412 CM

225 Industrial Park Road

Beaver, WV 25813

Issue Date: 1/1/2003 **LabDirector:** Claude Scott **Expiration Date:** 12/31/2003

Group: *Organics, VOCs Group I*

cis-1,2-Dichloroethylene	524.2		
trans-1,2-Dichloroethylene	524.2		
Benzene	524.2		Group Certified Except Vinyl Chloride
Carbon Tetrachloride	524.2		
Chlorobenzene	524.2		
1,4-Dichlorobenzene	524.2		
1,2-Dichlorobenzene	524.2		
1,2-Dichloroethane	524.2		
1,1-Dichloroethylene	524.2		
Dichloromethane	524.2		
1,2-Dichloropropane	524.2		
Ethylbenzene	524.2		
Styrene	524.2		
Tetrachloroethylene	524.2		
1,2,4-Trichlorobenzene	524.2		
1,1,1-Trichloroethane	524.2		
1,1,2-Trichloroethane	524.2		
Trichloroethylene	524.2		
Toluene	524.2		
Xylenes (Total)	524.2		
Vinyl Chloride	524.2	Certified	

Group: *Organics, VOCs Group II*

Dibromochloropropane (DBCP)	504.1	Certified

Group: *Organics, SOCs Group I*

Benzo(a)pyrene	550	Certified

Group: *Organics, SOCs Group II*

Di(2-ethylhexyl)adipate	525.2	Interim
Di(2-ethylhexyl)phthalate	525.2	Interim

Freedom_0006095_0209

REI Consultants, Inc.

00412 CM

225 Industrial Park Road

Beaver, WV 25813

Issue Date: 1/1/2003 **LabDirector:** Claude Scott **Expiration Date:** 12/31/2003

Group: *Inorgancis Group II*

Nitrite-N	300.0	Interim

Group: *Inorgancis Group III*

Fluoride	300.0	Interim

Group: *Inorgancis Group V*

Cyanide	335.4, SM4500CN-E	Certified

Group: *Organics, Pesticides Group I*

Endrin	508	Certified
Heptachlor	508	Certified
Heptachlorepoxide	508	Certified
Hexachlorobenzene	508	Certified
Hexachlorocyclopentadiene	508	Certified
Lindane	508	Certified
Methoxychlor	508	Certified
Chlordane	508	Certified
Toxaphene	508	Certified

Group: *Organics, Pesticides Group II*

Alachlor	507	Certified
Atrazine	507	Certified
Simazine	507	Certified

Group: *Organics, Pesticides Group III*

Aldicarb	531.1	Certified
Aldicarb sulfone	531.1	Certified
Aldicarb sulfoxide	531.1	Certified
Carbofuran	531.1	Certified

Group: *Organics, Pesticides Group VII*

Glyphosate	547	Certified

Group: *Organics, Haloacetic Acids (HAA5)*

Bromoacetic Acid	552.2	Certified
Chloroacetic Acid	552.2	Certified
Dibromoacetic Acid	552.2	Certified
Dichloroacetic Acid	552.2	Certified

Freedom_0006095_0210

REI Consultants, Inc.

00412 CM

225 Industrial Park Road

Beaver, WV 25813

Issue Date: 1/1/2003 **LabDirector:** Claude Scott **Expiration Date:** 12/31/2003

Group: *Organics, Herbicides*

2,4,5-TP (Silvex)	515.2	Certified
Dalapon	515.2	Certified
Dinoseb	515.2	Certified
Pentachlorophenol	515.2	Certified
Picloram	515.2	Certified

Group: *Organics, THMs*

Chloroform	524.2	Certified
Bromodichloromethane	524.2	Certified
Chlorodibromomethane	524.2	Certified
Bromoform	524.2	Certified
Total THMs	524.2	Certified

Freedom_0006095_0211

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

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Ex. 6 - Personal Privacy

Identification

Method Name: THALLIUM 2-8
Technique: Furnace
Method Desc: THALLIUM 2.00-8.00 PPB

Element: Tl
Instrument Model: 5100

Remarks:
LARRY A. DUFFIELD , CHEMIST 6-03-2003 100 ppm Pd+Mg MOD 2 INJ 1700C
IDL= 0.508 PPB MDL=0.648 PPB 6-03-03 LDR= 20.00 PPB 3-20-01

Instrument

Wavelength (nm): 276.8
Slit Width: 0.7

Read Time (sec): 6.0
Read Delay (sec): 0.0
BOC Time (sec): 2

Signal Type: Zeeman AA
Signal Measurement: Peak Area

Modified Spectrometer Settings: No

Calibration

Equations, Units, and Replicates:

Element	Calibration Equation	Calibration Units	Sample Units	Max Decimal Places	Max Significant Figures
Tl	Non-linear	µg/L	µg/L	3	4

Replicates: Fixed : 1

Sample
Sample Volume (µL): 20 **Diluent Volume (µL):** 5 **Diluent Location:** 0

Matrix Modifiers:	**Modifier 1**	**Modifier 2**
Volume (µL):	5	0
Location:	36	0
Add to blank and standards:	Yes	No
Add to reagent blank and samples:	Yes	No

	ID	Conc. (µg/L)	A/S Loc	Stock (µL)	Diluent (µL)
Calib. Blank	Calib Blank	----------	0	20	5
Reslope Std.	Reslope	4.00	39	20	5
Calib.Std. 1	STD 2.00 PPB	2.00	38	20	5
Calib.Std. 2	STD 4.00 PPB	4.00	39	20	5
Calib.Std. 3	STD 8.00 PPB	8.00	40	20	5

Freedom_0006095_0220

Furnace Conditions

Step. #	Temp (°C)	Ramp Time	Hold Time	Internal Flow	Gas Type	Read Step
1	130	2	22	300	Alternate	
2	130	1	35	300	Alternate	
3	1000	1	15	300	Alternate	
4	20	1	15	300	Alternate	
5	1700	0	5	0	Normal	X
6	2600	1	5	300	Normal	

Extraction System: No **Injection Temp. (°C):** 90

Furnace Clean-out ? No

Sequence

Step	Action and Parameters
A	Pipet diluent + modifier1 + spike + sample/std
B	Run furnace steps 1 to 2
C	Repeat sequence steps A to B 1 times
D	Run furnace steps 3 to end

Pipet Speed (%): 100

Checks

Check correlation coefficient? .....Yes
Minimum Correlation Coefficient: 0.99500
If coefficient is less than minimum: Repeat calibration 1 times and continue if OK.
If still not OK: Stop

Recalibrate instrument periodically? .....No

Analyze standards at end of run? .....No

Check Precision? .....No

Reanalyze samples beyond calibration range? ....Yes
Overcal Limit: 100 percent of Calibration Range.
Check Range On: Samples Recovery Samples
Dilute and reanalyze after: 1 Replicate
Alternate Sample Volumes (µL): 20 10 5 2 0
Use alternate volume blanks.
If spike greater than overcal limit, also reanalyze sample.

Perform matrix check calculations? .....No

Perform recovery measurements? .....No

Quality Control

QC Samples: Descriptions and Concentrations

	QC 1	QC 2	QC 3
QC Sample ID	IPC-4.00 PPB	QC BLANK	WSO34-2 2X QCS
Autosampler Loc	1	0	2
Count as a Sample	No	No	Yes
Use Reagent Blank	No	No	No
Concentration	4.000	0.000	3.100
Lower Conc Limit	3.800	-0.508	2.790
Upper Conc Limit	4.200	0.508	3.410

Freedom_0006095_0221

	QC 4	QC 5	QC 6
QC Sample ID	LAB RE BLANK	LFB 4.00 PPB	RLV-2.00 PPB
Autosampler Loc	3	4	5
Count as a Sample	No	No	Yes
Use Reagent Blank	No	No	No
Concentration	0.000	4.000	2.000
Lower Conc Limit		3.400	1.600
Upper Conc Limit	0.650	4.600	2.400

	QC 7	QC 8
QC Sample ID	IPC-4.00 PPB	QC BLANK
Autosampler Loc	1	0
Count as a Sample	No	No
Use Reagent Blank	No	No
Concentration	4.000	0.000
Lower Conc Limit	3.600	-0.508
Upper Conc Limit	4.400	0.508

Concentration Units: Calibration (µg/L)

Schedule for Analyzing QC Samples

	QC 1	QC 2	QC 3
QC Sample ID	IPC-4.00 PPB	QC BLANK	WSO34-2 2X QCS
After Initial Calib.	Yes	Yes	Yes
After Recalibration	No	No	No
Periodically	No	No	No
Frequency	1	1	1
At End	No	No	No

	QC 4	QC 5	QC 6
QC Sample ID	LAB RE BLANK	LFB 4.00 PPB	RLV-2.00 PPB
After Initial Calib.	No	No	Yes
After Recalibration	No	No	No
Periodically	No	No	No
Frequency	1	1	1
At End	No	No	No

	QC 7	QC 8
QC Sample ID	IPC-4.00 PPB	QC BLANK
After Initial Calib.	No	No
After Recalibration	Yes	Yes
Periodically	Yes	Yes
Frequency	10	10
At End	Yes	Yes

Periodic Timing of Analyses

Count: Samples

Frequency: Variable

Interrupt sample to analyze QC: Yes

Failure Actions for After-Calibration QC's

	QC 1	QC 2	QC 3
QC Sample ID	IPC-4.00 PPB	QC BLANK	WSO34-2 2X QCS
Times to Retry QC	1	1	1
When All Tries Fail	Recalibrate	Continue	Recalibrate
Optional Message			

	QC 4	QC 5	QC 6
QC Sample ID	LAB RE BLANK	LFB 4.00 PPB	RLV-2.00 PPB
Times to Retry QC	1	1	2
When All Tries Fail	Continue	Continue	Continue
Optional Message			

Freedom_0006095_0222

	QC 7	QC 8
QC Sample ID	IPC-4.00 PPB	QC BLANK
Times to Retry QC	None	None
When All Tries Fail	Recalibrate	Autozero
Optional Message		

Failure Actions for Periodic QC's

	QC 1	QC 2	QC 3
QC Sample ID	IPC-4.00 PPB	QC BLANK	WSO34-2 2X QCS
Times to Retry QC	1	1	None
When All Tries Fail	Continue	Continue	Continue
Optional Message			

	QC 4	QC 5	QC 6
QC Sample ID	LAB RE BLANK	LFB 4.00 PPB	RLV-2.00 PPB
Times to Retry QC	None	None	None
When All Tries Fail	Continue	Continue	Continue
Optional Message			

	QC 7	QC 8
QC Sample ID	IPC-4.00 PPB	QC BLANK
Times to Retry QC	1	1
When All Tries Fail	Recal & Rerun	Recal & Rerun
Optional Message		

Failure Actions for At-End QC's

	QC 1	QC 2	QC 3
QC Sample ID	IPC-4.00 PPB	QC BLANK	WSO34-2 2X QCS
Times to Retry QC	None	None	None
When All Tries Fail	Continue	Continue	Continue
Optional Message			

	QC 4	QC 5	QC 6
QC Sample ID	LAB RE BLANK	LFB 4.00 PPB	RLV-2.00 PPB
Times to Retry QC	None	None	None
When All Tries Fail	Continue	Continue	Continue
Optional Message			

	QC 7	QC 8
QC Sample ID	IPC-4.00 PPB	QC BLANK
Times to Retry QC	1	1
When All Tries Fail	Recal & Rerun	Continue
Optional Message		

Maximum Retries After QC Failure

Maximum allowed reanalyses: 2 **Action when maximum exceeded:** Stop

---

Options

Results Display/Printed Log - Modified Settings: Yes

Method Header

Method Name Element Method Description Complete Method

Date Technique Wavelength Lamp Current Sample Info File Name Calibration Equation Slit Width Energy

Results Header

Element Autosampler Location Date

Sample ID Sampler Volumes

Column Headings

Concentration Data: Conc. - Sample Units Conc. - Calibration Units

Absorbance Data: Blank Corrected Signal Peak Area Peak Height Bkgnd. Peak Area Bkgnd. Peak Height

Additional Parameters: Time Peak Stored Message

Freedom_0006095_0223

Data Categories
Data: Replicate Data Mean Data Statistics
Peaks: None
Summary: Calibration Curve Calibration Summary

Peaks to Save: Last Replicate for Each Sample

Freedom_0006095_0224

Element	IDL	FRW Level	MDL Day 1	MDL Day 2	MDL Day 3	MDL 3 Day $\bar{X}$	LDR Study (RL) Limit
Antimony ✓ ✓	0.42 ppb	0.84 ppb	0.66	0.58	0.61	0.84 ppb	6
		1.26 ppb	0.87	1.35	0.95	4-7-03	
Arsenic ✓ ✓	0.66 ppb	1.32 ppb	0.95	1.93	1.04	1.05 ppb	10
		1.98 ppb	0.86	0.92	0.62	4-16-03	
Barium ✓ ✓	~~.00039~~ ppm .00018	~~.00039~~ ppm	~~.00017~~	~~.000311~~	~~.000333~~	.0003	2
		.000269	.000242	.000529	.000320	7-10-02	
Beryllium ✓ ✓		0.06 ppb	0.04	0.05	0.06	0.05 ppb	4
		0.09 ppb	0.05	0.04	0.03	2-5-03	
Cadmium ✓ ✓	0.04 ppb	0.08 ppb	0.11	0.10	0.11	0.12 ppb	5
		0.12 ppb	0.15	0.11	0.11	1-21-03	
Copper ✓ ✓	0.18 ppb	0.36 ppb	0.19	0.18	0.28	0.32 ppb	50
		0.54 ppb	0.65	0.39	0.20	1-13-03	
Chromium ✓ ✓	0.29 ppb	0.58 ppb	0.45	0.36	0.54	0.51 ppb	100
		0.87 ppb	0.62	0.48	0.58	1-24-03	
Lead ✓ ✓	0.17 ppb	0.34 ppb	0.18	0.21	0.29	0.24 ppb	5
		0.51 ppb	0.27	0.29	0.17	1-7-03	
Mercury ✓ ✓	0.[illegible] ppb	0.098 ppb	neg 0.050	neg 0.073	0.036 ok	0.064 ppb	2 5.0 ug/l
		0.147 ppb	neg 0.075	0.098 ok	0.050 ok	4-18-03	6-3-03
Nickel ✓ ✓	0.39 ppb	1.38 ppb	0.52	0.68	0.68	0.62 ppb	
		2.07 ppb	0.70	0.63	0.51	4-4-03	
Selenium ✓ ✓	0.40 ppb	0.80 ppb	1.16	0.90	0.96	1.01 ppb	50
		1.20 ppb	1.10	1.01	0.90	5-2-03	
Thallium ✓ ✓	0.508 ppb	1.02 ppb	0.508	0.578	0.741	0.648 ppb	2
		1.52 ppb	0.561	0.620	0.879	6-3-03	
Aluminum ✓ ✓		1.5 ppb	2.23	1.71	3.09	2.1[illegible]	RL=3 = MDL too bouncy. Raise RL
		2.85	2.85	2.70	0.85	1-18-02	

Hg - negative numbers for IDL
Very poor recovery of spikes. Suggest higher spikes

Element	IDL	FRW Level	MDL Day 1	MDL Day 2	MDL Day 3	MDL 3 Day $\bar{X}$	LDR study Limit
Iron	.009 ppm	0.012 ppm	.005	.027	.011	0.014 ppm	
✓✓		0.024	.010	.009	.009	3-28-03	
		0.036	.026	.012	.014		
Manganese	.003 ppm	.009 ppm	.006	.006	.006	0.009 ppm	
✓✓		.018	.013	.007	.010	3-28-03	
		.027	.011	.009	.010		
Sodium	.03 ppm	.03 ppm	.09 neg value	.11	.05 neg value	0.08 ppm	Neg. values
✓✓		.06	.06	.09	.04	3-31-03	
		.09	.11	.08	.05		
Zinc	.004 ppm	.004 ppm	.010	.005	.012	0.009 ppm	
✓✓		.008	.011	.005	.008	4-7-03	
		.012	.010	.010	.007		
Silver	0.18 ppb	.36	.08	.225	.27	0.22	
✓✓		.54	.28	.23	.23	3-6-02	

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL SCIENCE CENTER
Analytical Services and Quality Assurance Branch
701 Mapes Road
Fort Meade, MD 20755-5350

July 16, 2003

Andrea M. Labik, Sc. D.
Director
West Virginia Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services
167 11th Avenue
South Charleston, West Virginia 25303-1137

Dear Dr. Labik:

The assessment team has competed the report resulting from the on-site review of WV's SDWA Laboratory Certification Program on June 25-26, 2003. We request that you provide a written corrective action plan to address the listed findings within 30 days of receipt of this report (August 18, 2003).

If you have any questions please call me at 410-305-2653 or E-mail (Slayton.joe@epa.gov).

Sincerely,

Joseph Slayton
Technical Director

cc:

Robin Costas (3ES20)
Richard Rogers (3WP22)
Charles Jones, Jr. (3ES10)
Wanda Johnson (3WP22)

SDWA Lab Certification Program:
On-Site Review

Rev.7-16-03

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory Section
167 11th Avenue
South Charleston, WV 25303

June 25-26, 2003

Robin Costas
Joseph Slayton

U.S.E.PA. - Region III
Analytical Services and Quality Assurance Branch
701 Mapes Road
Ft. Meade, Maryland 20755-5350

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Introduction:

On June 25-26, 2003 an on-site review was conducted of the West Virginia's SDWA Laboratory Certification Program of the West Virginia Department of Health and Human Resources, Bureau of Public Health, Office of Laboratory Services. Laboratory SDWA certifications for chemistry are conducted by Dr. Wayne Morganroth, Chemistry Laboratory Supervisor, Mr. Larry Duffield, Chemist II and Mr. Greg Young, Chemist II. Laboratory SDWA certifications for microbiology are conducted by Mr. Thomas Ong, Microbiologist Supervisor, and Ms. Tracy Goodson, Microbiologist III. Charlotte Billingsley, Associate Director oversees the Laboratory Certification Program and reports directly to Andrea Labik, Director Office of Laboratory Services.

This review was conducted through interviews, laboratory records/file review and the review of program Standard Operating Procedures (SOPs). A joint inspection with the WV Laboratory Certification Program was not conducted during this assessment to allow more emphasis on records review (data audit) and discussion with senior managment.

This program assessment was conducted by Robin Costas, Chemist and Joseph Slayton, Technical Director, USEPA, Region III, Analytical Services and Quality Assurance Branch, 701 Mapes Road, Fort Meade, Maryland 20755-5350.

Personnel/Training/Vacancies:

Since the last oversight review performed by EPA in 1999, an additional chemist has completed the Certification Officer's (COs) training course. Currently the WV program has two chemistry COs (Mr. Duffield and Dr. Morganroth) certified for inorganic and organic chemistry and one CO who just completed the certification course for inorganic chemistry (Mr. Young). Unfortunately, the loss of organic analysis capability from the Environmental Chemistry section in 1997 has not made it possible for the chemistry COs to gain hands-on experience with the SDWA methods for organics. As a result, the review of SDWA organic procedures requires methods review and preparation of checklists by the COs as part of the preparation for assessments.

The Microbiology section lost a CO just prior to the last Agency review in 1999. Ms. Joyce Vance-Abshire successfully completed the Certification Officer requirements for Microbiology (letter dated July 19, 1999 from Dr. M.K. Smith). However, Ms. Vance-Abshire has since left the laboratory and has been replaced with Tracy Goodson. Ms. Goodson was attending the COs course for microbiology during this on-site assessment.

It is planned that both Mr. Young and Ms. Goodson will be performing inspections jointly with

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the more experienced CO as part of their on-the-job training.

Also, since the last on-site review, Charlotte Billingsley has returned to the laboratory as Associate Director in a part time capacity.

Program Overview:

The WV Laboratory Certification Program is based upon the Manual for the Certification of Laboratories Analyzing Drinking Water, Criteria and Procedures Quality Assurance, EPA 815-B-97-001, March 1997 and upon the 40 CFR Part 141-143 SDWA requirements, as well as, the analytical methods referenced in these documents. This includes the requirement that laboratories successfully analyze at least one proficiency testing sample per analyte per method per year. All laboratories are also to have procedures and documentation, which are found satisfactory by an on-site inspection by State COs at least once every three years. All of the WV SDWA COs are trained professionals with years of laboratory experience (both Mr. Young and Ms. Goodson have about 4 years of bench experience).

Certification Program Documentation:

The WV laboratory microbiology certification program has developed an SOP/QA manual entitled: "Drinking Water Certification Program-Microbiology" (revision 8/21/01). This document includes the following topics: Introduction (cites various supporting federal regulations and the use of the EPA Lab Certification Manual as the focus for the WV Microbiological program); Laboratory Certification Officer (qualifications); Certification Parameters; Certification Renewal (table listing forms, mailing label files, etc.); On-site Evaluations (checklists, procedures, reports, follow-up, etc.); Adding a Certified Laboratory (In-State); Adding a Certified Laboratory (Out-of-State); Performance Evaluation Samples (indicated as "UNDERGOING MAJOR REVISION"); Records Retention and Storage; Drinking Water Laboratory Certification Renewal (form); Laboratory Information Form: Drinking Water Laboratory Certification Renewal *FINAL NOTICE* (form); Drinking Water Certificate; Water Survey Schedule (template to track projected on-site inspections); Presurvey Package (cover letter and pre-survey form); On-site Inspection Report (template); On-site Evaluation Checklist; Follow-up Letter (reminder notice template for response to the on-site inspection); Follow-up Letter (2) (template for responses that were not acceptable); tracking chart for on-site evaluations (tracking corrective actions and correspondence associated with on-site inspections); Application for Laboratory Certification (form); Letter in Response to Out-of-State applications (Note: includes WV's approach to "Reciprocity"); Letter Noting Receipt of Application (form letter); Key to List of Approved Tests (the WV Laboratory Certification Program groups analytes for certification); and a "Listing of Labs Certified in WV" (listed by analyte groups for both Microbiology and Chemistry).

The SOP for WV's Environmental Chemistry has been updated since the last on-site assessment. The Environmental Chemistry Standard Operating Procedures, Laboratory Certification Program

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(revision 4/20/02 approved 5/2/02) includes: Organization chart; criteria for certifying laboratories (general overview and requirements for SDWA certification, schedule for applications, on-sites and PT study participation); acceptance of NELAC accreditation; posting by April 1st of each year on web page of the certification status of WV SDWA laboratories (chemistry and microbiology); schedule for report issuance (within 4 weeks of the on-site) and corrective action reports from the laboratories (within 60 days); parameter groups (used for billing, since certification is by method and analyte); and certification of out-of-State laboratories (after review of PT results, certificate from primary state, copy of last on-site assessment, and copy of QM/QC protocols with first application).

Both the WV Chemistry and Microbiology certification programs have adopted a fixed schedule for PT participation by the laboratories (main study the first three months of the calender year) and any necessary make-up studies to occur with final PT based certification determined by the programs on October 1of each year. Both programs track PT performance and on-sites using tabular listings. Recently a data base has been developed which lists the certification status of each laboratory for chemistry and microbiology by method and analyte. An update for the microbiology certification program SOP is planned to include the new PT schedule/plan.

Observations:

Laboratory Certification Records Management:

The documentation for the Microbiology and Chemistry Certification Program was complete and well organized. These records allowed the review of PT data, on-site reports, corrective actions and certification status and offical communications. The PT program is well documented and the laboratories have been officially notified of the schedule and procedures (both microbiology and chemistry). Schedules of PTs and on-sites and certification issuance are tracked and organized in tabular form. Much progress has been made in this area by the Chemistry program since the last EPA assessment (records for microbiology certifications continue to be excellent). As per the recommendation from the last EPA program assessment, the return/addition of the Associate Director and administrative assistant/clerk support have significantly improved records management in the chemistry certification program. Much work was completed by Dr. Morganroth and Ms. Billingsley.

On-site Laboratory Inspections:

All required on-site assessments and follow-up corrective actions and communications have been completed by microbiology. However, despite quarterly updates to EPA during the first two years since the last program review and despite repeated promises, the problem of not performing the required on-site inspections continues for chemistry. During this EPA review, it was suggested that past problems with scheduling the shared State vehicle should not be a significant problem in the future as the vehicle is scheduled further in advance. It was suggested that the shortage in chemistry COs should be greatly helped with the new CO addition. Also,

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during this assessment it was pointed out that the great majority of SDWA analyses required for the WV program are conducted by commercial laboratories. It was stressed that on-site reviews of commercial chemistries laboratories should be made a priority to assure the quality of drinking water in West Virginia.

Findings & Suggestions:

1. On-site Laboratory Inspections:

Finding: Though several laboratories have dropped out or have been decertified for chemistry, of the eight remaining in- State laboratories in the program, the on-sites for three laboratories are greatly overdue. (All three were last assessed in 1997-making them three years overdue for an assessment and six years total since the last visit by WV laboratory certification personnel). **Suggested Corrective Action:** During the closing meeting with the Laboratory Director, Associate Director and lead chemistry CO, the necessity for completing these on-sites was stressed. These must be conducted as soon as possible particularly since the laboratories continue to be listed on the WV web page as fully certified. In the future, laboratories which are due for an on-site and have not had one within the 3 year cycle (any over one year overdue) should be decertified by the WV program.

2. WV Web page (www.wvhdhhr.org):

a. Finding: A discussion with Victor Wilford, Environmental Health Services, indicated that it is critical that the web site listing of laboratories certified by WV be accurate since the water utilities are instructed to employ such laboratories for SDWA analyses. Unfortunately, this important source of information is not being kept up to date (last updated March 2002). Since that time, it was indicated that several laboratories have lost their WV SDWA certifications and should not be listed on the WV web site at all, e.g., Reliance Analytical Services, Inc. (Hedgesville, WV), as a result of a WV on-site assessment on July 25, 2001. **Suggested Corrective Action**: During the closing briefing of this assessment it was agreed that the WV program engineers would be notified by Email as soon as possible of the laboratories that should not be listed on the web site. Also, it was agreed that the web site would be updated with regard to de-certified laboratories as soon as possible.

b. Finding: The web site lists certification only by parameter group, e.g., Trace Metals group I and II, and not by method and analyte/s. **Suggested Corrective Action**: It was agreed during the closing meeting of EPA's assessment, that Laboratory Services would complete the necessary upgrade to the web page that will allow the page to list (or point to files containing) laboratory certification status by method and analyte.

3. Certification of Out-of-State Laboratories:

Finding: The certification of out-of-State laboratories represents a considerable drain on

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resources. It was pointed out that this work is justified for microbiology since the laboratories are near the borders of neighboring states and do a significant amount of WV SDWA work. However, the amount of chemical analyses being done by out-of-State laboratories is unknown. **Suggested Corrective Action:** It is suggested that Laboratory Services work with the WV Environmental Health Services program managers to determine if the amount of work sent to out-of-State laboratories, and based upon that information, determine whether the certification of these laboratories for chemistry should be continued. It is suggested that future applications for WV certification should include a listing of water supplies for which the laboratory has performed work for in the past or is projected to perform work for in the future. If this portion of the chemistry certification program is unnecessary, removing it or reducing it should help direct available resources to conduct the necessary work for in the in-State laboratories.

4. Scope of Certification/Approval:

Finding: The listing of laboratory certifications and approvals provided by Laboratory Services for chemistry do not include the full scope of the SDWA program and also include certifications which are not provided by Laboratory Services. **Suggested Corrective Action**: Laboratory Services should work with the WV Environmental Health Services program managers to determine possible additional areas for certification and/or approval, e.g., alkalinity, bromate, calcium, chlorite, conductivity, orthophosphate, pH, turbidity, silica, Specific Ultraviolet Absorption (SUVA) and TOC. Also, consideration should be given to dropping radiochemistry and asbestos from the listing.

5. Additional Suggestions:

a. Efforts should be continued to clean-out outdated milk records and other files in microbiology file cabinets to make room to allow organization and filing of out-of-State microbiology laboratory certification records (same organization/records management as for in-state laboratories).

b. Clerical help is needed in the microbiology section. Valuable time of professionals is spent filing and organizing the many records associated with laboratory certification, microbiological analysis records, and bottle requests.

c. Consideration should be given to requiring all records/information exchanges with the SDWA laboratories to be electronic. This would speed the process and provide an efficient method to easily organize records (in directories).

d. The Environmental Chemistry Standard Operating Procedures, Laboratory Certification Program (revision 4/20/02 approved 5/2/02) needs page numbers and section numbers.

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Assessors:

JS for RC 7/16/03

Robin Costas Date

7/16/03

Joseph Slayton Date

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL SCIENCE CENTER
Analytical Services and Quality Assurance Branch
701 Mapes Road
Fort Meade, MD 20755-5350

July 28, 2003

Andrea M. Labik, Sc. D.
Director
West Virginia Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services
167 11th Avenue
South Charleston, West Virginia 25303-1137

Dear Dr. Labik:

The assessment team has competed the reports resulting from the on-site SDWA review of your laboratory conducted on June 24-25, 2003. We request that you provide a written corrective action plan to address the listed findings within 30 days of receipt of this report (August 29, 2003).

If you have any questions please call me at 410-305-2653 or E-mail (Slayton.joe@epa.gov).

Sincerely,

Joseph Slayton
Technical Director

cc:

Robin Costas (3ES20)
David Russell (3ES20)
Richard Rogers (3WP22)
Charles Jones, Jr. (3ES10)
Wanda Johnson (3WP22)

Final On-Site Laboratory Evaluation Report (SDWA)

Inorganic Chemistry

(Rev. 7-25-03)

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory Section
4710 Chimney Drive, Suite G
Charleston, WV 25302

June 24-25, 2003

Surveyed by:

Joseph Slayton
Robin Costas

U.S.E.P.A. - Region III
Analytical Services and Quality Assurance Branch
701 Mapes Road
Ft. Meade, Maryland 20755-5350

A. Introduction:

On June 24-25, 2003 an on-site inspection of inorganic chemistry was conducted of the West Virginia Department of Health and Human Resources, Bureau for Public Health, Office of Laboratory Services. The chemical analyses of drinking water samples is conducted at a separate location, Environmental Chemistry Laboratory Section, 4710 Chimney Drive, Suite G, Charleston, WV 25302. The purpose of this inspection was to determine the capability of the laboratory to perform its mission as it relates to the Safe Drinking Water Act (SDWA). The laboratory was represented by Dr. Andrea Labik, Sc.D, Office of Laboratory Services Director, Charlotte Billingsley, Associate Director, Dr. Wayne Morganroth, Laboratory Section Supervisor, Mr. Larry Duffield, Chemist II (analysis of metals), and Mr. Greg Young, Chemist II (analysis of inorganic, non-metal analytes).

This inspection was conducted by: Robin Costas, Chemist (evaluation of metals) and Joseph Slayton, Technical Director (evaluation of inorganic, non-metals); USEPA, Region III, Analytical Services and Quality Assurance Branch, 701 Mapes Road, Ft. Meade, Maryland 20755-5350.

The laboratory lost the capability to perform the analyses of organic contaminants for SDWA in 1997. These analyses are performed by commercial laboratories certified by West Virginia. Efforts are underway to regain this analytical capability. Any assistance by the EPA Region 3 Water Protection Division would be greatly appreciated, as expertise in organic analyses would not only provide a valuable technical assistance for the SDWA laboratories in WV, but also greatly improve WV ability to oversee and certify these laboratories. WV requested that this on-site review include the review of alkalinity, cyanide and pH to expand the scope of their inorganic certification. The listing in Section E of this report, "Contaminant Method Information" is the regulated and "unregulated" parameters for which the laboratory is requesting SDWA certification and approval.

A number of the inorganic analytes require "cool, 4°C" preservation (alkalinity, conductivity, cyanide, nitrite, nitrate, TDS, Turbidity, Sulfate). All inorganic analytes with the exception of nitrite are not cooled during transport to the laboratory. The samples collected by Environmental Health Services are described as not being for compliance purposes but for engineering purposes, e.g., double check on the distribution system. As a corrective action for the last on-site assessment, the laboratory routinely labels the results for such unpreserved samples as "Sample >4 Celsius, Not Valid for SDWA Compliance Reporting".

SDWA samples for total nitrate are routinely analyzed and reported as a sum for (NO2+NO3)-N. The State uses a concentration of 0.5 mg/L to "trigger" the immediate re-sampling and re-analysis, i.e., this may indicate an NO2-N concentration of 0.5 mg/L which has a maximum concentration limit of 0.5 mg/L.

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B. Personnel:

The courtesy and professionalism of the laboratory personnel was greatly appreciated by the inspection team. It was apparent from the excellent record keeping and quality control procedures, that the laboratory personnel are dedicated to achieving analytical excellence.

C. Proficiency Testing (PT) Samples:

The laboratory data for Proficiency Testing samples for the years 2000 thru 2003 were discussed during the on-site evaluation. The laboratory results were "Acceptable" for all regulated inorganic parameters reported with the exception of the following "Not Acceptable" results: April 2003 - conductivity (successful makeup audit in June 2003); January 2001 - turbidity, manganese, aluminum (successful makeup audit July 2001). **This is an excellent record of performance and indicates the laboratory's results are accurate and reliable.**

D. Analytical Method References:

The list of parameters in Section E were audited during this inspection with the associated methodology cited as follows:

(SM) - Standard Methods for the Examination of Water and Wastewater, 18th edition.
(EPA83) - Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79/83.
(EPA93) - Determination of Inorganic Substances in Environmental Samples, Aug 1993, EPA/600/R-93/100.
(EPA94) - Methods for the Determination of Metals in Environmental Samples, May 1994, EPA/600/R-94/111.
(CLADW) - Manual for the Certification of Laboratories Analyzing Drinking Water, March 1997, EPA 815-B-97-001.

E. Contaminant Method Information: *Primary Inorganic Chemicals, Parameters in the Lead and Copper Rule, Sodium and Turbidity:*

Parameter	Method	Instrumentation
Antimony	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Arsenic	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Barium	ICP (EPA94, 200.7)	Varian Liberty 100
Beryllium	GFAAS (SM 3113B)	Varian SpectraAA - 400 Plus
Cadmium	GFAAS (SM 3113B)	Varian SpectraAA - 400 Plus
Chromium	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Copper	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Lead	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Mercury	Cold Vapor AA (EPA94, 245.1)	PE-50B W/PE CVAAS
Selenium	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Sodium	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Thallium	GFAAS (EPA94, 200.9)	Perkin-Elmer 5100, HGA 600

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Primary Inorganic Chemicals, Parameters in the Lead and Copper Rule, Sodium and Turbidity (Continued):

Parameter	Method	Instrumentation
Alkalinity	Titration (SM 2320B)	25 mL Buret
Conductance	Conductance (SM 2510B)	Model 31 Conductivity Bridge
Cyanide	Ion Selective Electrode (SM 4500CN-F)	Orion Model EA 940 Meter Orion ISE and Double Junction Reference
Fluoride	Ion Chromatography (EPA93, 300.0)	Dionex-120
Nitrate	Automated Cadmium (EPA93, 353.2)	Technicon Auto-Reduction Analyzer II
Nitrite	Automated Cadmium (EPA93, 353.2)	Technicon Auto-Reduction Analyzer II
pH	Electrometric (EPA83, 150.1)	Corning 430 Meter & 3-In-One Electrode
Turbidity	Nephelometric (EPA93, 180.1)	Hach 2100A Turbidimeter

Optional Primary Contaminants:

Parameter	Method	Instrumentation
Nickel	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Total Hardness	Titration (SM 2340C)	25 mL Buret

Secondary Contaminants:

Parameter	Method	Instrumentation
Aluminum	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Iron	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Manganese	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Silver	GFAAS (SM 3113B)	Varian SpectrAA - 400 Plus
Zinc	Flame AA (SM 3111B)	Varian SpectrAA - 400 Plus
Chloride	Ion Chromatography (EPA93, 300.0)	Dionex-120
Sulfate	Ion Chromatography (EPA93, 300.0)	Dionex-120
TDS	Gravimetric (SM 2540C)	Gelman A/E GF Filters; Blue M Oven; Mettler AG-245

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F. Calibration & Detection Information:

Maximum Contaminant Level (MCL), Method Detection Limit (MDL), Reporting Limit (RL as defined by the WV Laboratory.)

Primary Contaminants; Lead and Copper Rule; Sodium and Turbidity:

Contaminant	***Calibration Standards*** **(mg/L)**	**MCL(mg/L)**	**MDL(ug/L)**	**RL(ug/L)**
Metals:				
Antimony	BLK; 0.003; 0.006; 0.012	0.006	0.84	3
Arsenic	BLK; 0.002; 0.005; 0.010; 0.020	0.050	1.05	2
Barium	BLK; 0.50; 5.00; 10.0	2.00	0.0003	5
Beryllium	BLK; 0.0002; 0.0005; 0.001; 0.002	0.004	0.05	0.2
Cadmium	BLK; 0.001; 0.002; 0.004	0.005	0.12	1
Chromium	BLK; 0.001; 0.0025; 0.005; 0.010	0.100	0.51	1
Copper	BLK; 0.001; 0.0025; 0.005; 0.010	1.3*	0.32	1
Lead	BLK; 0.001; 0.0025; 0.005; 0.010	0.015*	0.24	1
Mercury	BLK; 0.0002; 0.0005; 0.001; 0.002	0.002	0.064	0.2
Selenium	BLK; 0.002; 0.005; 0.010	0.050	1.01	2
Sodium	BLK; 2.0; 5.0;10.0;15.0;20.0	20.0+	0.08	2000
Thallium	BLK; 0.002; 0.004; 0.008	0.002	0.65	1
Non-Metals:				
Cyanide	BLK; 0.05; 1.25; 0.2; 0.3; 0.4	0.2	3.6	50
Fluoride	BLK; 0.1; 0.2; 0.50; 1.00	4.0	6	100
Nitrate	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	10.0	3.6	50
Nitrite	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	1.0	4.8	50
	Cd Column Check Standard (1.0)			
pH	4.0; 7.0; 10.0 (pH Units)	[6.5-8.5]	-	-
TDS	NIST Traceable Std. Wts.	[500]	-	-

* "Action Level"
\+ "Reportable Level"
[ ] = Suggested MCL (SMCL)

G. Quality Control (QC) Procedures:

The laboratory follows a "Manual of Quality Assurance, Environmental Chemistry", (QA Manual, Rev. 2003). This document includes: QA plan and policy statement; laboratory organization; employee job descriptions and responsibilities; sampling instructions; sample handling procedures; reporting of results; chain of custody (formal internal tracking is limited to cases which may involve litigation); quality assurance monitoring; analytical procedures; data reduction; data verification; data validation; data reporting; preventive maintenance; internal QC

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checks; precision and accuracy; sample rejection policy; and proficiency testing. A partial list of the QC procedures observed during this inspection included: calibration records for thermometers; on-going temperature records of refrigerators and drying ovens; analysis of an external (2nd source) QC sample with each analytical batch; method detection limit determinations; duplicate analysis (precision measure); spike analysis (accuracy/recovery measure); blank analysis/batch; check standards at 10% frequency (instrument drift measure); instrument "run logs"; cadmium column reduction efficiency measured and recorded; standard weights employed to verify balance performance; detailed/clearly written and quickly retrieved analytical records; on-going compilation and charting of QC check results; and the resistance/conductivity of lab pure water recorded each day of use.

H. Analytical Deviations:

Deviations are those laboratory techniques not in compliance with the mandatory requirements of the analytical methods cited above or with the 1997 EPA Manual for the Certification of Laboratories Analyzing Drinking Water, Fourth Edition, EPA/815-B-97-001, (CLADW). In addition, procedures/techniques, which are considered critical by the inspectors for the production of quality data are cited as "Good Laboratory Practices" (GLP). The following changes are required for the laboratory to be in compliance with the SDWA program (40 CFR 142.10).

General:

1. The principle WV state SDWA laboratory must maintain capability and certification for all the contaminants specified in the State Primary Drinking Water Regulations, p. E-1 CLADW, unless the State has been granted waivers for compliance monitoring of these analytes or has contracted with laboratories which are SDWA certified (by EPA or by a state other than WV such as Lancaster Laboratories, Pennsylvania) for these analytes. A listing of commercial laboratories that are employed by the State program for SDWA compliance monitoring for the analytes not measured at the WV Lab and their current SDWA Certification status (signed copies of the certificates from other state/s) is necessary to complete our records. Also, in the future as new certificates are issued to these laboratories, electronic copies should be routinely forward to the certification officer.

2. The inorganic non-metal results are routinely qualified "not valid for SDWA compliance reporting". However, on several occasions the results were not flagged (samples 30039-turbidity; 30021-alkalinity, pH, sulfate, and TDS). It is suggested that the "#" code be added to all temperature dependent analytes which are not chilled during transport as a part of the "Inorganic Chemistry Analysis Report" template. In addition, the "@" indicating exceedance of holding time should be added directly to the form for pH results.

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pH:

3. The results from duplicate pH analyses should not be averaged unless the complex mathematical procedure for taking the average of logarithmic numbers (GLP) is used. It is suggested that instead of using an average, the pH result with the greatest difference from 6.5-8.5 be reported.

Ion Chromatography:

4. The bench record (instrument printout) needs include the initials of the analyst and date to supplement the initials and date printed by the software (GLP).

Turbidity:

5. A check standard (IPC) is required to be analyzed at the beginning, at 10% frequency and at the end of the analyses set (EPA 180.1).

I. Recommendations:

These items are offered as suggestions (not required):

a. Extensive work has been performed with the routine conductance of MDL studies. When next performed consideration should be given to increasing the spike level to help assure reasonable percent recoveries of the analytes (for example 60-140% or other target limit set by the laboratory). The MDL should be about 3 fold lower than the reporting limit (ie., the concentration of lowest calibration standard). The reporting limit should be less than the SDWA Maximum Contaminant Limit (MCL) for the analyte.

b. Although, the QA Manual is extensive and well written, the next time that the manual is updated the following items described in the CLADW should be considered and procedures documented: a process to determine data quality objectives (driven by use of data by clients); listing of all SOPs (title, date, status) used in the laboratory; traceability of calibration material (primary and second source); certificate retention for reference weights, reference thermometers and reference materials; create "QS Components Table" which lists all parameters analyzed indicating dates for last MDL, IDP, SOP, PT, and internal review; laboratory policy for calculating MDL and IDP data; laboratory policy for dropping outlier data from MDLs, IDPs, and calibrations (should rely directly on observations of laboratory accidents and statistical tests for outliers); frequency of recertification of reference weights and thermometers; action limits for the calibration of mechanical pipets; the listings of corrective actions for failed QC checks should be expanded to include what should be done when acceptable QC cannot be achieved (e.g., do not report the data or qualify the result as an estimate with an indication of the direction of bias); pollution prevention (steps taken to reduce the harmful impact of analyses); policy for the analyses of PT samples (i.e., analyzed as a routine samples using the same QC frequency and

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limits); management system review (yearly review of Quality System by upper management);

c. Although, the Laboratory QM describes "internal audits", these reviews are not being performed. Internal review is regarded as a key component of a laboratory's quality system to ensure continuous improvement, so these audits should be initiated and conducted on a set schedule. In addition, data verification, should be routinely performed (review and spot checking of 10% of the data with sign off by a second analyst).

d. Consideration should be given to the purchase of cyanide stock material, as the titration procedure to standardize the material is very technique dependent.

e. A separate refrigerator is recommended for the storage of samples separate from calibration and QC materials.

f. Consideration should be given to analyzing MDLs at 1/year frequency when the methods state "should" for more frequent MDL studies. It is suggested that fortified blanks carried through the entire method at the quantitation level be performed yearly as a more critical method performance study (e.g., recoveries should be 40-160% until laboratory determined limits are developed).

g. The practice of recording the sample temperatures in the determination of conductance should be continued since it was determined by the laboratory to be the source of PT difficulty.

h. Sample tags are date-stamped upon receipt and log-in by the laboratory. The initials of the sample custodian should be recorded on the tag as well.

i. It is suggested that the frequency of balance verifications should be increased to be done with each analyses when weight critical measurements are made (preparation of calibration stocks, gravimetric analyses, such as TDS, mechanical pipet checks, and when small quantities < 100 mg are measured). The reference weights should be stored in a desiccator.

j. The newly initiated procedure for recording of the calibration of thermometers in a log book (previously recorded only on a thermometer tag) should be continued.

k. At the time of this assessment no samples had been analyzed for cyanide. When samples arrive for this analysis, the field removal of residual chlorine must be checked and recorded (preservation information).

l. The laboratory should develop a records management system, i.e., each SOP, notebook, QM, etc., is assigned a unique number and the status of the documents are recorded, e.g., initiation date, status (draft, in progress, complete, active, archived).

m. Efforts to update the inorganic non-metal SOPs to include details of corrective actions for failed QC should be continued. The tabulation in the SOP for metals may prove a useful model.

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n. A reference should be provided in future SOP updates to indicate the source of the QC limits. If these are based on "in-house limits" (cases when the reference methods do not specify limits), the rationale should be provided and supporting data should be collected to allow a systematic determination.

o. A reagent log should be created for the metals analytical work.

p. In instances where standards are used passed their expiration date, a second source audit should be used that has not expired.

q. It is apparent that a great deal of time and coordination is needed to maintain the metals laboratory because of the number of instruments involved. Consideration should be given to obtaining an ICP-MS which could replace most, if not all, of current instrumentation for a more efficient work environment.

J. Certification Status:

Certified: <u>Upon correction of the items listed as findings, "Certified" will be recommended for</u>:

Metals:
Arsenic; Antimony; Barium; Beryllium; Cadmium; Chromium; Copper; Lead; Mercury; Nickel, Selenium; Sodium; and Thallium.

Inorganic Non-Metals:
Alkalinity; Conductance; Cyanide; Fluoride; Nitrate; Nitrite; pH; Turbidity; and Hardness.

Secondary Analytes: <u>Upon correction of the items listed as findings, "Fully Acceptable" will be recommended for:</u>

Metals:
Aluminum; Iron; Manganese; Silver; and Zinc.

Inorganic Non-Metals:
Chloride; Sulfate; and TDS.

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K. Inspectors:

7/28/03

Joseph Slayton Date

7.28.03

Robin Costas Date

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On-Site Laboratory Evaluation Report (SDWA)

Date of Report: July 15, 2003

Microbiology

Environmental Microbiology Section
Office of Laboratory Services
Bureau for Public Health
West Virginia Department of Health and Human Services
167 11th Avenue
South Charleston, WV 25303

Date of Assessment: June 24-25, 2003

by

David E. Russell

U.S. Environmental Protection Agency, Region III
Office of Analytical Services and Quality Assurance
701 Mapes Road
Fort Meade, MD 20755-5350

A. Introduction:

On June 24-25, 2003, an evaluation of the Environmental Biology Section of the Office of Laboratory Services in Charleston, West Virginia, was conducted to determine the capability of the Laboratory to perform its mission as it relates to the Safe Drinking Water Act. The Laboratory was last evaluated in December 1999.

The Environmental Microbiology Section (hereafter, the Laboratory) is currently analyzing drinking water for total coliform and fecal coliform (or *Escherichia coli*) using Multiple Tube Fermentation (MTF) or Colilert. Although not performed routinely, the Laboratory also has the capability to analyze drinking water using Membrane Filtration (MF). In addition, Heterotrophic Plate Counts (HPC), using the pour plate method, are regularly performed, but not on drinking water compliance samples. The Laboratory wishes to maintain certification for all four methods: MTF, Colilert, MF, and HPC.

The Laboratory is to be congratulated for the record of PT sample analysis it has established over the past three years. In 2001, 2002, and 2003 the Laboratory successfully analyzed PT sample sets using the MTF, Colilert, and MF methods. All three methods were evaluated each year.

The equipment and procedures employed in the bacteriological analyses of drinking water by this laboratory conform with the provisions of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA, as corrected or amended by the Errata distributed November 18, 1998), except as described in Sections C and D below.

B. Personnel:

The following personnel currently analyze drinking water for total coliforms, fecal coliforms, (or *E.coli*), or heterotrophic plate count.

Tom Ong	Microbiologist Supervisor
Mike Flesher	Microbiologist III
Tracey Goodson	Microbiologist II
Joe Cochran	Microbiologist II
Debbie Walker	Laboratory Assistant II

The Assessors wish to thank these individuals for their willing assistance and cooperation during the on-site evaluation. Tom Ong was especially helpful and generous with his time.

C. General Findings:

General Findings include specific incidences of non-conformance with the equipment and analytical procedures required by the *Manual for the Certification of Laboratories Analyzing*

Drinking Water, 4th Edition (1997, U.S. EPA, as corrected or amended by the Errata distributed November 18, 1998), or laboratory procedures that, in the opinion of the assessor, jeopardize the generation of valid data.

There are no General Findings.

D. Recommendations:

The following remarks are offered as suggestions to help improve the quality and integrity of the data the Laboratory generates. Note that all paragraph numbers and quotes are from Chapter V of the *Manual for the Certification of Laboratories Analyzing Drinking Water*, 4th Edition (1997, U.S. EPA) unless otherwise indicated.

1. The Federal Register (40 CFR 74(a)(1) footnote 2) requires that source water collected for analysis for total coliforms, fecal coliforms, or HPC must be held below 10°C in transit and analysis must be initiated within 8 hours. The difficulty here lies in determining whether or not the source water samples are true "compliance" samples, a designation that would make meeting the above conditions mandatory. It is strongly recommended that the Laboratory always error on the side of producing scientifically and legally defensible data, and accordingly, treat all source or raw water samples as "compliance" samples. Therefore, whether raw samples are marked as "compliance" samples or not, if either condition above (<10°C or 8 hour holding time) is not met, the results should be flagged as "Not Valid for SDWA Compliance Reporting". At the time of the on-site visit, the Microbiology Supervisor agreed to this procedural change, and immediately informed staff of the new procedure.

2. The Federal Register (40 CFR 141.21(f)(3) footnote 2) in regard to the collection of drinking water samples from distribution systems, states, "Systems are encouraged but not required to hold samples below 10°C during transit." Accordingly, it is recommended that distribution system samples be held below 10°C during transit and that this condition be documented through the use of a temperature blank, the temperature of which would be determined upon arrival at the Laboratory and recorded.

3. The autoclave quality control and maintenance records detailed in paragraph 3.5.3 should be clearly associated with a specific identifiable autoclave. Suggest clearly labeling autoclaves with numbers and recording the autoclave numbers with all quality control and maintenance data.

4. Although the current record of spore strips used in the quality control of autoclaves (paragraph 3.5.4) shows the results for both the test and control strips, they are not clearly labeled as such. The table could be easily improved by enlarging it and adding labels.

5. Paragraph 8.4.3 specifies "person(s) responsible for performing analysis" as one of the

information items that should be included in laboratory records. The Laboratory's media and dilution water final pH values are recorded in the media prep log by taping the pH meter printout onto a separate logbook page. This represents a separate record of media QC data, and as such, should be initialed by the analyst in order to introduce more accountability into this QC record. The only other analyst initials in this logbook are those initials on the autoclave performance printout taped to other pages. The autoclave record, media prep record, and final pH record, are not always entered into the logbook by the same person, underscoring the need for initials.

6. According to paragraph 3.4.1, incubator "thermometers should be placed on the top and bottom shelves of the use area". In the Laboratory's large free-standing Environette incubator, the two thermometers are on adjacent shelves. They should be on shelves well separated from one another (if not the top and bottom shelves) so as to provide a better representation of the incubator's internal temperature.

7. The record of QC for sterilization of sampling bottles should be organized by batch of bottles, with each batch occupying one line in the logbook. Such a system would allow for the appropriate corrective action to be taken when the QC check of sterilization (testing a single bottle from the batch) fails. The corrective would be to reprocess all the bottles in the batch. The addition of a "Comments" column in the logbook would allow space for recording the corrective action taken. If this QC record is kept by batch, then the corrective action can be easily carried out. An ideal process would involve recording all the bottle numbers in each batch, so the composition of each batch is always known.

8. It is recommended that positive and negative results of all laboratory quality control checks be recorded in the same way. Either as "present" or "absent", or "+" or "-".

9. The log of the IDEXX bottle volume QC should show the actual volume measured and the initials of the person performing the QC. The procedure should involve filling the IDEXX bottle to the 100ml mark, then pouring that volume into the class "A"graduated cylinder to determine the actual volume represented. A tolerance of plus or minus 2.5% is allowed. Alternatively, the bottle volume could be checked by <u>weighing</u> a bottle filled to the 100ml mark (100mls will weigh 100gs). The weighing technique would allow one to record accurately a value exceeding 100ml, whereas the use of a graduated cylinder does not.

10. IDEXX bottles loaded with sodium thiosulfate are not necessary because sufficient thiosulfate is added to sample bottles when they are prepared. IDEXX bottles without the sodium thiosulfate are much less expensive. If the IDEXX bottles are ever used as sample bottles, then they must contain the sodium thiosulfate.

11. Paragraph 4.3.2 (as amended by the Errata distributed 11/18/98) states that the regular QC of the laboratory reagent water should include the Bacteriological Quality test (annually) if the water does not meet the criteria of Type II reagent water as described in *Standard Methods*

for the Examination of Water and Wastewater, 18th Edition, Section 1080). Those criteria include a conductivity below 1.0 umho/cm @ 25°C. The conductivity of the Laboratory reagent water is above 1.0 umho/cm @ 25°C several times each year, indicating it does not meet the requirement for Type II water. Consequently it is recommended, in accordance with paragraph 4.3.2, that the Bacteriological Quality test (or "Suitability Test") be performed annually.

12. Currently, sample receipt and analysis data is recorded on three different forms with no one form containing all the information. The three forms are 1) the Water Bacteriological Report, 2) printout of spreadsheet kept in three-ring binders, and 3) final spreadsheet, not printed, but stored in the computer. This record could be improved by consolidating this information into one complete record, containing, as specified in paragraph 8.4, the times analyses are begun and ended. The new form from the engineering division may improve the situation but not represent the best solution.

13. The laboratory should be commended for the effort it is making to record the times associated with the analysis of drinking water, e.g., time sample analysis initiated or results read. The lack of this documentation was a concern included in the 1999 on-site visit report. These times provide documentation that the correct procedures were followed adding to the legal defensibility of the data. It is recommended that the laboratory include all times documenting that the correct procedures were followed, including the times at which initial and subsequent analyses are begun and results read.

14. It is recommended that the neutralization of the residual chlorine of finished drinking water samples be checked routinely. A randomly-selected portion of these samples each month (e.g., 10%) should be tested with a drop of iodine solution for excess sodium thiosulfate which will be present if all residual chlorine was neutralized. The iodine drop test could be easily performed (by a second analyst) on the sample water remaining in the collection bottle once the 100 mL test volume was removed. The sodium thiosulfate reacts with the iodine to produce sodium tetrathionate and sodium iodide both of which are colorless; consequently, the amber color produce by the drop of iodine quickly disappears. If sodium thiosulfate is not present the amber color remains.

15. The Laboratory should be commended for revising the Water Bacteriological Report form to include a check box labeled "NOT VALID FOR SDWA COMPLIANCE REPORTING". It is suggested that in a future revision of the form, check boxes for the reasons a report might not be valid for SDWA reporting be included. Those reasons would include exceeding holding time, failure to ship samples at less than 10°C (source water for any analysis or finished water for HPC), and collection of compliance samples by individuals not authorized to do so. Something similar already exists on the form to explain why samples were rejected and not examined. Such explanation serves to inform those who submit samples.

16. It is recommended that the Laboratory continue to participate in the training of samplers,

particularly in the completion of the Water Bacteriological Report form. Several hundred completed forms from 2002 and 2003 were examined by the assessor. One of the most common errors in completion of the form was the sampler's failure to indicate the type of sample collected. This occurred on sample numbers 011281, 011190, 011072, and 010943, all collected in Kanawha County in early 2003.

17. The Environmental Microbiology Quality Assurance Plan (latest revision date 5/17/00) was reviewed. The QAP does not reflect changes in laboratory procedures that have been implemented as a result of the 1999 on-site evaluation. For example, the laboratory now uses a unique identifying number on each sample bottle to link sample collection data to the sample, yet the QAP does not describe this procedure. The QAP should be updated to include all changes in procedure resulting from on-site assessments, past and present. Overall, the QAP should be updated periodically, at an interval specified in the document. It is further recommended that the clerical assistance necessary to keep the QAP up to date be provided to the Laboratory.

E. General Comments:

1. The Microbiology Supervisor is to be commended for the immediate steps taken to instruct staff to flag all source or raw water sample results as "Not Valid for SDWA Compliance Reporting" when such samples are not held below 10°C during transit or exceed the 8 hour holding time. This will be done whether it is known such samples are "compliance" samples or not.

2. Several important processes have been improved since the last on-site visit, including a) marking each sample bottle with a unique number and recording that number on the Water Bacteriological Report, b) documenting a demonstration of analytical competence for each new analyst, and c) tracking calibrations of thermometers by devoting a single log page to each thermometer. An atmosphere of continual improvement is evident at the Laboratory.

3. The Laboratory maintains detailed quality control records that includes data above and beyond that required by the SDWA manual. Examples include use of two max./min. thermometers with each autoclave run, bimonthly autoclave maintenance, and weekly spore strip testing of autoclave performance.

4. The Laboratory is to be commended for revising the Water Bacteriological Report form since the last on-site, incorporating all the requirements listed in paragraph 6.5, and adding a check box to be used when the test result is "NOT VALID FOR SDWA COMPLIANCE REPORTING". Review of records indicated that this check box is indeed used, particularly when the 30 hour holding time is exceeded, an occurrence that appears to happen only rarely.

5. The Laboratory is also to be commended for the routine practice of rejecting samples (without analysis) for exceeding the holding time, insufficient volume, insufficient

information on report form (such as collection date), unauthorized collector, residual chlorine, and insufficient air space to facilitate mixing.

F. Conclusions:

The Laboratory's management and staff are to be commended for their dedication to maintaining high standards in microbiological analysis and remaining committed to continual improvement. As shown in the table below, full certification will be recommended for Multiple-Tube Fermentation, Colilert, and Membrane Filtration. In accordance with 40 CFR 141.74, certification to perform total coliform analysis means the Laboratory is also certified to perform Heterotrophic Plate Counts (HPC).

G. Certification Status (Recommended by the Certification Officer):

Organisms	Technique	Method[1]	Certification Status
Total Coliforms, Fecal Coliforms (or *E. coli*)	Colilert	SM 9223	Full Certification
	Multiple Tube Fermentation	SM 9221B,E	Full Certification
	Membrane Filtration	SM 9222B	Full Certification
Heterotrophic Bacteria	Heterotrophic Plate Count	SM9215B	Full Certification

H. Assessor: For D.R. 7/28/03

David E. Russell
Microbiological Assessor

[1] *Standard Methods for the Examination of Water and Wastewater*, 19th Edition.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL SCIENCE CENTER
Analytical Services and Quality Assurance Branch
701 Mapes Road
Fort Meade, MD 20755-5350

September 4, 2003

Andrea M. Labik, Sc. D.
Director
West Virginia Department of Health & Human Resources
Bureau for Public Health
Office of Laboratory Services
167 11th Avenue
South Charleston, West Virginia 25303-1137

Dear Dr. Labik:

The assessment team has completed the review of the corrective action reports for the on-site assessment of the WV's Laboratory Certification Program (8/21/03) and the WV Health Laboratory (8/29/03), prepared in response to our on-site assessment reports (dated July 16, 2003 for the program review and July 28, 2003 for the laboratory review). We have the following comments:

Laboratory Review (findings for Inorganic Chemistry, no findings for Microbiology):

General:

Corrective action for finding #1: EPA's Office of Ground Water and Drinking Water (OGWDW, Cincinnati), has pointed out that drinking water analyses (compliance analyses) for WV's Office of Environmental Health Services (OEHS) must be performed by laboratories that are certified by EPA or by a State other than WV. We need to have copies of the signed certificates from other state/s to complete our records. We had underlined this part of the finding in our report, however the listing provided with the corrective action report includes a number of laboratories that list only WV certification. It is suggested that this item needs to be added to the agenda for discussion with the OEHS, e.g., Ms. Linda Keller, Assistant Manager of Regulatory Development and Compliance. OGWDW cites the Federal Register for this requirement (2002 CFR 141.11 vi on page 564).

Corrective action for finding #2: The response is fine, we will add a copy of the "Inorganic Chemistry Analysis Report" to our files when received.

Corrective action for finding #3: The response is fine, we will add a copy of updated SOP to our files when received.

Corrective action for finding #4: The response is fine, we will add a copy of the example

instrument printout with analyst's initial/date to our files when received.

Corrective action for finding #5: The response is fine.

Program Review (Comments from EPA were provided via E-mail (8/28/03) with the following open items listed in **bold print**):

Finding #1. Concerning on-site laboratory inspections, the response and plan look fine. **Please routinely provide copies of the inspection reports to the EPA review team as each is finalized. This will help track progress with the projected schedule.**

Finding #2. Concerning www.wvdhhr.org, the response is fine.

Finding #3. Concerning out-of-state laboratories, the response is fine. We understand the legal issues of dropping laboratories currently certified. However, consideration should be given to not renewing these laboratories after their current cycle. **Please forward the decision/s on this issue from the meeting of the Office of Laboratory Services and the Office of Environmental Health Services.**

Finding #4. Concerning the scope of certification/approvals for the WV Lab Cert Program, **please forward the decision/s on this issue from the meeting of the Office of Laboratory Services and the Office of Environmental Health Services.**

Finding #5. Concerning "Additional Suggestions", please provide information regarding item "a" and "b", which concern microbiology. This information was received on 8/29/03 with a follow-up return E-Mail (9/2/03), urging additional clerical help for microbiology to afford the organization of out-of-state laboratory certification records comparable with the filing system for the in-state laboratories.

Upon receipt of the listed information/materials we will issue an updated certification report for inoganic chemistry and will close out the on-site assessment (laboratory and program office). If you have any questions please call me at 410-305-2653 or E-mail (Slayton.joe@epa.gov).

Sincerely,

Joseph Slayton
Technical Director

cc:

Robin Costas (3ES20)
David Russell (3ES20)
Richard Rogers (3WP22)
Charles Jones, Jr. (3ES10)
Wanda Johnson (3WP22)

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Ex. 5 - Deliberative

January 11, 2007

Joe Slayton
USEPA - ASAQB
701 Mapes Road
Fort Meade, MD 20755-5350

At the request of our customer, enclosed is a final report for ERA's WatR™ Supply Proficiency Testing (PT) Study, WS-124. This laboratory has also received a copy of the attached final report with their individual evaluations. This report is intended for use by you and your customer's facility in evaluating all results they submitted to ERA.

All analytes in the WatR™ Supply Proficiency Testing Study, WS-124, have been evaluated using the following tiered approach. If the analyte is listed in the most current National Environmental Laboratory Accreditation Conference (NELAC) PT Field of Testing tables, the evaluation was completed by comparing the reported result to the acceptance limits generated using the criteria contained in the NELAC FoPT tables. If the analyte is not included in the NELAC FoPT tables, the reported result has been evaluated using the procedures outlined in ERA's Standard Operating Procedure for the Generation of Performance Acceptance Limits (SOP 0260).

If you have any questions regarding this report please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Quality Assurance Director, at 1-800-372-0122.

Sincerely,

Shawn Kassner
Proficiency Testing Manager

Curtis Wood
Quality Assurance Director

6000 West 54th Ave., Arvada, CO 80002 800-372-0122 fax (303) 421-0159 www.eraqc.com

WS-124 Definitions & Study Discussion

Study Dates: 11/06/06 - 12/21/06 **Report Issued: 01/11/07**

WS Study Definitions

The Reported Value is the value that the laboratory reported to ERA.

The ERA Assigned Values are compliant with the most current USEPA/NELAC FoPT Tables. A parameter not added to the standard is given an Assigned Value of "0" per the guidelines contained in the USEPA's Criteria Document and NELAC standards.

The Acceptance Limits are established per the criteria contained in the most current USEPA/NELAC FoPT Tables, or ERA's SOP for the Generation of Performance Acceptance Limits™ as applicable.

The Performance Evaluation:

Acceptable	= Reported Value falls within the Acceptance Limits.
Not Acceptable	= Reported Value falls outside the Acceptance Limits.
No Evaluation	= Reported Value cannot be evaluated.
Not Reported	= No Value reported.

The Method Description is the method the laboratory reported to ERA.

WS Study Discussion

ERA's WatR™Supply Proficiency Testing Study has been reviewed by ERA Senior Management and certified compliant with the requirements of the USEPA's National Standards for Water Proficiency Testing Studies Criteria Document (December 1998), and the criteria contained in the most currrent NELAC FoPT Tables.

ERA's WatR™Supply Study standards were examined for any anomalies. A full review of all homogeneity, stability and accuracy verification data was completed. All analytical verification data for all analytes in the standards met the acceptance criteria contained in the USEPA's National Criteria Document for Water Proficiency Testing Studies, December 1998, and the criteria contained in the most current NELAC FoPT Tables.

The data submitted by participating laboratories was also examined for study anomalies. There were no anomalies observed during the statistical review of the data.

ERA's WatR™Supply Study reports shall not be reproduced except in their entirety and not without the permission of the participating laboratories. The report must not be used by the participating laboratories to claim product endorsement by any agency of the U. S. government.

If you have any questions regarding ERA's WatR™Supply Proficiency Testing program, please contact Shawn Kassner, Proficiency Testing Manager, or Curtis Wood, Quality Assurance Director, at 1-800-372-0122.

ACCREDITED
Lab Code: 1539-01

Study: **WS-124**

ERA Laboratory Code: **W213401**

Laboratory Name: **West Virginia Dept of Health**

Inorganic Results

ACCREDITED
Lab Code: 1538-01

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ENVIRONMENTAL RESOURCE ASSOCIATES®
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WS-124 Final Complete Report

Larry Duffield
Program Manager I
West Virginia Dept of Health
4710 Chimney Dr, Suite G
Environmental Chemistry Lab
Charleston, WV 25302
304-965-2694

EPA ID: WV00003
ERA Laboratory Code: W213401
Report Issued: 01/11/07
Study Dates: 11/06/06 - 12/21/06

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
Mercury							
0006	Mercury	µg/L	4.87	4.88	3.42 - 6.34	Acceptable	EPA 245.1

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL SCIENCE CENTER
Analytical Services and Quality Assurance Branch
701 Mapes Road
Fort Meade, MD 20755-5350

December 20, 2006

Andrea M. Labik, Sc. D.
Director
West Virginia Department of Health & Human Resources
Bureau of Public Health
Office of Laboratory Services
167 - 11th Avenue
South Charleston, West Virginia 2503-1137

Dear Dr. Labik:

The final reports for the SDWA on-site assessment of your laboratory and WV's Laboratory Certification program were dated 10/24/06. The corrective action report from Larry Duffield, dated November 20, 2006 (additional materials received 12/7/06 for turbidity) addressed all remaining issues except for mercury and thallium. There were not corrective actions necessary for microbiology and the certification program as only suggestions were provided in the reports. Attached please find the certification update report for inorganic chemistry which reflects the provided corrective actions.

The analyses of SDWA compliance samples should not be performed for thallium using EPA 200.9 until another instrument is available. Also, compliance samples for mercury should not be analyzed until the necessary performance studies are complete and approved for the new instrument and a successful WS PT completed. As there may well be some delay regarding thallium and mercury, I am closing out this assessment. We will update certification for Hg and thallium when the necessary corrective actions are completed and documentation provided.

Sincerely,

Joseph Slayton
Technical Director

cc:
Wanda Johnson (3WP22)
Robert Lange (3WP32)
Charles Jones, Jr. (3EA00)
Robin Costas (3EA20)
George Long (3EA20)
David Russell (3EA20)

On-Site Laboratory Evaluation Update Report (SDWA)

Inorganic Chemistry

(Rev. 12-19-06 JS)

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory Section
4710 Chimney Drive, Suite G
Charleston, WV 25302

On-site: September 19-20, 2006

Surveyed by:

Robin Costas
George Long
Joseph Slayton

U.S.E.P.A. - Region III
Analytical Services and Quality Assurance Branch
701 Mapes Road
Ft. Meade, Maryland 20755-5350

Recommended Certification Status:

Based upon the corrective action report dated November 20, 2006 and December 7, 2006 from the September 19-20, 2006 SDWA on-site assessment, the assessment team recommends the following SDWA certification status for organic chemistry.:

LEGEND

C – Certified NA - Not Acceptable
AP – Approved
NP - Not Approved

CONTAMINANT	ON-SITE REVIEW	
		Method
Antimony	C	SM 3113B
Arsenic	C	SM 3113B
Barium	C	EPA200.7
Beryllium	C	SM 3113B
Cadmium	C	SM 3113B
Chromium	C	SM 3113B
Copper	C	SM 3113B
Copper	C	SM 3111B
Cyanide	C	SM 4500 CN F
Fluoride	C	EPA300.0
Lead	C	SM 3113B
Mercury	NC	EPA245.1
Nitrate	C	EPA353.2
Nitrite	C	EPA353.2
Selenium	C	SM 3113B
Thallium	NC	EPA200.9
Chloride	AP	EPA300.0

Sulfate	AP	EPA300.0
TDS	AP	SM2540C
Manganese	AP	SM 3111B
Nickel	AP	SM 3113B
Zinc	AP	SM 3111B
Aluminum	AP	SM 3113B
Iron	AP	SM 3111B
Silver	AP	SM 3113B

LEAD AND COPPER RULE:

CONTAMINANT	ON-SITE REVIEW 11/30/99	
		Method
Lead	C	SM3113B
Copper	C	SM3113B
Copper	C	SM 3111B
pH	C	EPA150.1
Conductivity	C	SM2510B
Calcium or Calcium Hardness as $CaCo_3$	C	SM3500 CAD
Alkalinity	C	SM2320B
Sodium	C	SM3111B
Turbidity	C	EPA180.1

Inspectors:

Robin Costas 12/19/06

George Long 12/19/06

Joseph Slayton 12/19/06

CETAC Hg Analysis Report

Analyst: Pat Marchio pm
Worksheet file: C:\Program Files\QuickTrace\Worksheets\112006b.wsz
Date Started: 11/20/2006 9:57:29 AM
Comment:

Ex. 5 - Deliberative

COPY

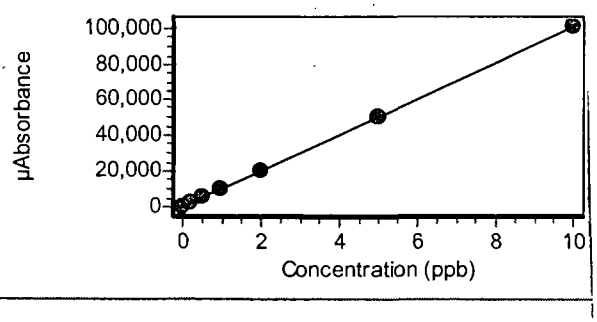
11-20-06

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags	DF
Calibration Blank					STD	11/20/06 10:09:57 am	0.000000	268	7.52		1.00
Replicates	270.9	270.6	240.5	289.1							
0.2 ppb					STD	11/20/06 10:12:43 am	0.200000	2165	1.07		1.00
Replicates	2151.9	2150.7	2156.7	2199.0							
0.5 ppb					STD	11/20/06 10:15:29 am	0.500000	5464	1.75		1.00
Replicates	5350.2	5419.9	5533.5	5552.0							
1.0 ppb					STD	11/20/06 10:18:16 am	1.000000	10512	1.45		1.00
Replicates	10297.3	10540.6	10553.5	10656.3							
2.0 ppb					STD	11/20/06 10:21:04 am	2.000000	20294	0.36		1.00
Replicates	20265.9	20386.8	20306.5	20216.4							
5.0 ppb					STD	11/20/06 10:23:51 am	5.000000	50826	1.56		1.00
Replicates	50150.5	50197.8	51175.7	51780.5							
10.0 ppb					STD	11/20/06 10:27:36 am	10.000000	100575	0.34		1.00
Replicates	100300.9	100253.5	100833.3	100913.5							

Calibration

Equation: A = 345.005 + 10036.820C
R2: 0.99998
SEE: 195.4849
Flags:



Ex. 5 - Deliberative

ICV 5.0 ppb					ICV	11/20/06 10:31:45 am	5.204000	52582	1.12
Replicates	52051.5	52393.0	53423.0	52458.8					
% Recovery	104.09								

ICV was unnecessarily repeated below

11/20/2006 11:28:07 AM 112006b.wsz

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags	DF
Single: ICV 5.00 ppb					ICV	11/20/06 10:37:43 am	4.929000	49814	0.97		1.00
Replicates	49359.6	49649.8	49748.5	50498.7							
% Recovery	98.58										
ICB					ICB	11/20/06 10:45:24 am	-0.013440	210	9.38		1.00
Replicates	210.5	194.0	237.7	198.1							
JT Baker 5.0 ppb LCS					LCS	11/20/06 10:50:06 am	5.357000	54108	2.45		1.00
Replicates	52342.0	53875.9	54897.2	55316.4							
% Recovery	107.13										
Prep Blank					PBK	11/20/06 10:53:48 am	0.026100	607	3.47	Q	1.00
Replicates	590.3	614.1	590.0	633.6							
						< 2.2 X MDL - Passed					
MRL 0.20 ppb					UNK	11/20/06 10:56:34 am	0.187700	2229	0.99		1.00
Replicates	2196.3	2241.9	2236.5	2241.8							
						%R = 93.8					
LFB-MRL 0.2 ppb					UNK	11/20/06 10:59:23 am	0.217800	2531	0.56		1.00
Replicates	2530.5	2541.5	2510.6	2540.3							
						%R = 108.9					
LFB 2.0 ppb					UNK	11/20/06 11:02:09 am	2.023000	20651	0.16		1.00
Replicates	20605.4	20653.3	20677.4	20669.8							
						%R = 101.2					
CCV 5.0 ppb					CCV	11/20/06 11:04:57 am	5.099000	51518	1.12		1.00
Replicates	50925.7	51251.0	51623.0	52271.6							
% Recovery	101.97										
CCB					CCB	11/20/06 11:08:34 am	-0.014820	196	7.39		1.00
Replicates	190.3	216.8	194.8	183.1							
060404 (WS-124)					UNK	11/20/06 11:11:22 am	4.872000	49240	0.14		1.00
Replicates	49139.9	49284.1	49283.0	49253.0							
						= 4.87 µg/L					
060404 DUP					DUP	11/20/06 11:14:11 am	4.848000	49007	0.20		1.00
Replicates	48871.1	49005.4	49072.5	49079.9							
		RPD 0.48									
060404 MSK					MSK	11/20/06 11:17:01 am	6.746000	68058	0.29		1.00
Replicates	67790.5	68031.2	68177.6	68232.6							
% Recovery	94.90										

Freedom_0006095_0265

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags	DF
060404 MDUP					MSDUP	11/20/06 11:20:41 am	7.069000	71294	0.20		1.00
Replicates	71095.3	71288.1	71370.6	71420.5							
% Recovery	111.02	RPD 4.67									
CCV 5.0 ppb					CCV	11/20/06 11:24:19 am	5.292000	53458	0.47		1.00
Replicates	53434.2	53215.0	53374.6	53806.4							
% Recovery	105.84										
CCB					CCB	11/20/06 11:27:55 am	-0.013120	213	3.75		1.00
Replicates	207.4	221.6	205.6	218.7							

Notes

MDL (11/17/06) = 0.020 ppb

Linear Dynamic Range (10/27/06) = 35 ppb

LFB and matrix spike concentration = 2.0 ppb

Freedom_0006095_0266

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)
16.50	23.25		

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0267

PBK

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0070

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0070

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Stop analysis

DUP

Concentration (ppb)	Low Limit (ppb)	High Limit (ppb)	RPD
0.2000	0.2000	10.0000	20.0000

Failure flag: D

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0268

MSK

Concentration (ppb)	Low Limit %	High Limit %
2.0000	70.0000	130.0000

Failure flag: N

Error action for manually inserted QC: Stop analysis

MSDUP

Concentration (ppb)	Low Limit %	High Limit %	RPD
0.0000	70.0000	130.0000	20.0000

Failure flag: D

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0269

Ex. 5 - Deliberative

West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Section

COPY

Standard Operating Procedure

Mercury Cold Vapor Atomic Absorption Standard Operating Procedures Using EPA Method 245.1

Prepared by: Patrick Marchio Date: 10-10-06
Patrick Marchio, Chemist I

Reviewed by: Larry Duffield Date: 10-4-06
Larry Duffield, Program Manager

Approved by: Andrea M Labik Date: 10-10-06
Dr. Andrea Labik, Laboratory Director

Periodic Review:

Signature	Title	Date

Freedom_0006095_0271

Table of Contents

Section page

1. Summary of Method.....3
2. Interferences.....3
3. Equipment, Supplies, and Reagents.....3
4. Sample Handling and Preparation.....5
5. Quality Controls and Standards..... 6
6. Procedure and Data Analysis..... 9
7. Maintenance.....12
8. Safety Precautions.....13
9. References.....13

Appendix page

A. Quality Controls and Corrective Action Summary.....14
B. EPA Alternative Test Procedure letter.....16
C. Software Deviations from Method Quality Controls and Sample Labels.....17

Freedom_0006095_0272

Mercury Cold Vapor Atomic Absorption Standard Operating Procedures Using EPA Method 245.1

1. Summary of Method

This method is used to measure total mercury (organic and inorganic) in drinking, surface, ground, sea, brackish waters and industrial and domestic wastewater. The range of this method used in this SOP is 0.2 to 10.0 µg/ L mercury (Hg). This is a reduced volume method that uses the same molar equivalents of reagents as listed in the EPA method. A 40 ml aliquot of a water sample is transferred to a 50 ml plastic digestion tube. The sample is then refluxed/ digested in a diluted potassium permanganate-potassium persulfate and acid solution and oxidized for 2 hours at 95 °C in a block digester. Mercury in the digested sample is then reduced with stannous chloride to elemental mercury. The mercury vapor from the sample is separated by a gas liquid separator and swept into an absorption cell mounted in the instrument with inert argon gas. The instrument makes absorbance readings based on a 253.65 nm wavelength using a CCD detector. This SOP contains alternate labels for quality controls that vary from the method labels. The purpose of these alternate labels is for automated calculations by the software.

2. Interferences

2.1. Interferences have been reported for waters containing sulfide, chloride, copper, and tellurium. Organic chemicals which have broad ultra-violet absorbance are confirmed interferences.

2.2. Volatile materials (e.g. chlorine) which absorb at 253.7 nm will cause a positive interference. Volatiles will come out of solution when samples are digested. Samples sit in the autosampler racks without caps allowing volatiles to escape into the air.

2.3. Ambient background mercury.

3. Equipment, Supplies, and Reagents

3.1. Equipment

- 3.1.1. Cetac M-6100 Cold Vapor Mercury Analyzer with autosampler
- 3.1.2. Digi-Prep block digester with temperature controller, see Appendix B for a letter of approval from the EPA.
- 3.1.3. Computer, software, and printer.
- 3.1.4. Calibrated thermometer checked annually against an NIST certified thermometer.
- 3.1.5. Analytical balance and weighing boats
- 3.1.6. Several bottle top reagent pipet dispensers.
- 3.1.7. Regulator and metering valve for Argon gas set to deliver gas at 40 psi with a flow of 125 ml/min.
- 3.1.8. Flowmeter capable of measuring 125 ml/min.

3.2. Supplies

- 3.2.1. Several 100, 250, 500 and 1000 ml class A volumetric flasks.

All glassware used in this procedure must be rinsed with 1+1 HNO_3 and Type I water.

3.2.2. 10, 50, 100, and 1000 µl adjustable pipettes with pre-cleaned tips.

3.2.3. 50,100 ml Class A graduated cylinders.

3.2.4. Several 50 ml Class A plastic digestion tubes with screw caps from SCP Scientific

3.2.5. Several 25 ml plastic autosampler tubes

3.2.6. 5 and 20 ml class A glass pipets.

3.2.7. pH paper

3.2.8. Peristaltic pump tubes

3.2.9. Compressed Ultra High Purity Argon gas

3.3. Reagents and Standards

3.3.1. ASTM Type I Reagent water with a resistivity ≥ 18.0 megohms/cm. If less, replace cartridges. The resistivity must be verified each day of use and recorded.

3.3.2. HNO_3 – Trace Metals grade

3.3.3. H_2SO_4 – Trace Metals grade

3.3.4. HCl - Trace metals grade

3.3.5. Potassium permanganate ($KMnO_4$) crystals- reagent grade

3.3.5.1 $KMnO_4$ solution – Dissolve 50 g. of $KMnO_4$ in 1 liter of reagent water in a class A volumetric flask.

3.3.5.2 This is also used to fill the mercury vapor scrubber on the back of the instrument.

3.3.6. Potassium persulfate ($K_2S_2O_8$) crystals- reagent grade

3.3.6.1 $K_2S_2O_8$ solution – Dissolve 50 g of $K_2S_2O_8$ in 1 liter of reagent water. in a class A volumetric flask.

3.3.7. Sodium chloride (NaCl) crystal – reagent grade

3.3.8. Hydroxlyamine hydrochloride ($NH_2OH{\cdot}HCl$) – reagent grade

3.3.8.1 Sodium chloride- Hydroxlyamine hydrochloride solution – Dissolve 120 g of each of the above reagents into 1 liter of reagent water in a class A volumetric flask.

3.3.9. Stannous chloride ($SnCl_2{\cdot}\ H_2O$) – reagent grade

3.3.9.1 10% $SnCl_2{\cdot}\ H_2O$ solution in 7% HCl: Add 25 g of $SnCl_2{\cdot}\ H_2O$ to a 250 ml volumetric flask half full of reagent water containing 17.5 ml concentrated HCl, dilute to volume and swirl to mix. To make 500 ml of this solution, dissolve 50g $SnCl_2{\cdot}\ H_2O$ into a 500 ml class A volumetric flash half full containing 35 ml HCL, then dilute to volume and swirl to mix. The use of HCl is allowed in Standard methods, 18th Edition - SM3112B, and was approved by EPA auditor Robin Costas.

3.3.10. Lab Reagent Blank (LRB) – prepare by dispensing reagent water into a 1 liter plastic jug, add 2 ml of HNO_3,shake to mix and let stand 16 hrs. before use. Document in logbook.

3.3.11. Mercury Stock Standards - Ultra Scientific 1000µg/ml Hg

3.3.11.1 Intermediate Standard 1.0 ppm – To a 100 ml class A volumetric flask half full, add 0.15 ml of conc. HNO_3. Add 100 µl of 1000µg/ml stock standard and dilute to volume. Invert several times to mix. Date and record in standards prep logbook. This standard should be prepared fresh each day of use.

3.3.12. Laboratory Control Sample (LCS) stock also known as Quality Control Sample(QCS) – J.T. Baker 1000µg/ml Hg

3.3.12.1 LCS intermediate Solution 1.0 ppm- To a 100 ml class A volumetric flask half full, add 0.15 ml of conc. HNO_3. Add 100µL of 1000µg/ml stock LCS standard and dilute to volume. Invert several times to mix. This standard is used to prepare the quality control sample. Date and record in standards prep logbook. This standard should be prepared fresh each day of use.

3.3.13. Rinse water for the autosampler consists of a 1% solution of each HCl and HNO_3.

3.3.14. Rinse water for the GLS and pump tubes consist of a 5% solution of HCL.

3.3.15. 2-Propanol – used to clean the windows of the absorption cell.

4. Sample Handling and Preparation

4.1. Receiving- Samples received for metals analysis should be in an approved 1 liter or 1 quart pre-cleaned container, preferably plastic, and supplied by our lab. Samples not received in approved containers can be rejected. All samples are logged in and numbered. Samples should be received in lab within 2 weeks of collection, no ice required.

4.2. Preservation- Our lab does not recommend field preservation of metals samples due to hazards of acid and contamination. Unpreserved samples must be acidified upon receipt with 2 ml. concentrated nitric acid per liter volume. Mix thoroughly by capping and shaking. Note acidification with a blue "A" with date and time on cap. To ensure pH <2, check with pH test paper after sample has been allowed to set for 16 hours. If the pH is >2 add an additional 2 ml of HNO_3 and retest the pH after holding the sample for an additional 16 hrs. Document in Acidification/Digestion Logbook.

4.3. Holding Time- Following acidification, sample must be held for 16 hours before further processing. Preserved sample holding time is 28 days from time of collection.

4.4. Calibration standards and Sample preparation

4.4.1. Begin by pipetting the following amounts of the 1.0 ppm mercury standard (3.3.11.1) into 100 ml volumetric flasks half full of reagent water and containing 150 µl concentrated HNO_3

Standard	Volume of 1.0 ppm Hg standard used
Calibration Blank	0.0
0.2 ppb	20 µl
0.5 ppb	50 µl
1.0 ppb	100 µl
2.0 ppb	200 µl
5.0 ppb	500 µl
10.0 ppb	1000 µl

4.4.2. Dispense 40 ml of each standard using a 50 ml Class A graduated cylinder into a 50 ml plastic digestion tube.

4.4.3. Add 2.0 ml of H_2SO_4 and 1.0 ml HNO_3 to the standards in the plastic digestion tubes, and allow to cool.

4.4.4. LCS preparation – prepare in the same manner as the above 5.0 ppb standard following steps 4.4.1 thru 4.4.3 using the LCS intermediate solution(3.3.12.1)

4.4.5. Prepare samples by dispensing a 40 ml aliquot of preserved sample into a plastic digestion tube using a class A graduated cylinder, then adding 2.0 ml of H_2SO_4 and 1.0 ml HNO_3, and allow to cool.

4.4.5. LFBs and Matrix spikes

4.4.5.1. Add 80 µL of 1.0 ppm Hg standard (3.3.11.1) to 40 ml aliquot of LRB labeled (LFB), and to all sample matrix spikes (MS). The resulting spike level will be 2.0 ppb ok

4.4.5.2. LFB at the MRL – Add 8 µL of 1.0 ppm Hg standard (3.3.11.1) to 40 ml aliquot of LRB labeled LFB-MRL. ok

4.4.6. To all the digestion tubes add 6.0 ml of the $KMnO_4$ solution (3.3.5.1). Swirl to mix. Wait 15 min

4.4.7. To all the digestion tubes add 3.2 ml of the $K_2S_2O_8$ solution (3.3.6.1). Swirl to mix.

4.5. Digestion procedure

4.5.1. Digest only the **LRBs, LFBs, MS, MSDs, IDCs and all sample unknowns and spikes.**

4.5.2. Tightly screw caps onto plastic digestion tubes and place into the block digester.

4.5.3. Digest the above samples and QCs at 95°C. Begin by turning on the block digester at the control panel and set it to heat up to 95 °C, allow it to warm up and verify the temperature ± 2 °C using a calibrated thermometer placed in a tube with water at the same volume through a hole in a cap. Make adjustments to the temperature as necessary to achieve a digestion temperature of 95°C. Once to temperature, set the unit's timer for 2 hours. Samples will then digest for this amount of time and the unit will automatically shut off if programmed to.

4.6 After samples have digested and cooled, add 2.4 ml of Sodium chloride- Hydroxlyamine hydrochloride solution (3.3.8.1.)

4.7. Records- Records on each step of sample handling, i.e., receipt, acidification, digestion, completion, must be kept for each sample and entered in the sample prep logbook for this purpose.

5. Quality Controls and Standards

5.1. Initial Demonstration of Capability (IDC) – Before using this method to analyze drinking water, operator must determine or perform:

5.1.1. Linear Dynamic Range (LDR) - The upper limit of the LDR must be established for each analyte at each wavelength utilized. Determine this from readings from a minimum of six different concentration standards across the range, two of which are close to the upper limit of the LDR. LDRs must be documented and kept on file. The upper LDR limit should be an observed signal no more than 10% below the true value level extrapolated from the calibration standards. LDRs should be verified whenever there is a significant change in analytical performance.

5.1.2. Instrument Detection Limit (IDL) –Take ten consecutive measurement readings of the calibration blank. Determine standard deviation between readings and

multiply by 3. This is the IDL in ppm. Re-evaluate as deemed necessary. Record in QC book.

5.1.3. Method Detection Limit (MDL) – This is the minimum concentration with 99% confidence that it is greater than zero. Determine annually. Analyze seven replicates of Fortified Reagent Water (FRW) (See 5.4.5.) at 2-3 times the IDL concentration. FRW must be processed through entire analytical method including digestion. Repeat analysis of all 7 replicate aliquots over 3 days. Determine standard deviation between readings of 7 replicates, multiply this by 3.14, this gives the MDL in ppm. Use the mean of 3 non-consecutive days of analyses. Negative values of FRW readings are not valid.

5.1.4. Demonstration of Precision and Accuracy - It is determined by each analyst initially before analyzing compliance samples by analyzing four replicates of a known amount of analyte that has been put through the entire sample handling and preparation process. The accuracy limits is ±10% of true value. The precision acceptance limits for the IDC is < 10% RSD, if > 10% RSD then repeat analysis and/or re-make the IDC solution. The IDC solution is prepared from a second source standard, one not used to calibrate the instrument.

5.1.5. Analysis of an unknown with a recovery of +/- 10 % of true value.

5.2. Procedural Notes

5.2.1 Correlation Coefficient – This is calculated from the concentration of standards used in the calibration and their corresponding absorbance values. If it is greater than or equal to 0.995 continue analysis, if less than 0.995 stop and correct the problem and recalibrate. Record the correlation coefficient on raw data sheet.

5.2.2. Annual Proficiency Testing – Analyst must participate in annual Proficiency Testing study mandated by EPA. This involves analysis, using approved methods, of an unknown sample from a private vendor approved by EPA. Successful recovery of Hg is mandatory to retain certification. If it is not successfully recovered, method must be reviewed to determine cause and corrected. A Corrective Action Report must be forwarded to the Region 3 Certifying Authority. Participation in subsequent study will then be required with successful recovery expected for analyte in question.

5.2.3. Dilutions – If sample concentration is higher than highest calibration standard, sample must be diluted and reanalyzed until it is within calibration range. Prepare by taking an aliquot of digested sample and dilute with the calibration blank solution. Make note of dilution factor and apply when calculating concentration for reporting.

5.2.4. Reporting results – Results of analysis are to be reported as mg/l in three significant figures. If analyte quantity is less than the lowest calibration standard then report as "less than" (<) that standard concentration. Report date of analysis, analyst's initials, and method used.

5.2.5. Calculations – All calculations for analyte recovery and QC results whether performed automatically by computer or done manually must be accessible for review and kept on file for at least five years.

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5.2.6. Data Reports – Raw data reports generated by instrument during analysis must be separated by year and kept on file for review for at least five years.

5.2.7. Quality Control Records – All results of quality control analysis must be recorded in a QC binder for that element. Results must be tabulated and LFBs graphed in appropriate charts to show relationship to previous data. If results appear consistently high or low, problem should be investigated, corrected, and documented.

5.2.8. The software of the computer system utilizes nomenclature that varies slightly from the EPA method quality control names. Using the software's designated names allows it to automatically calculate percent recoveries of standards and matrix spikes, and relative percent difference of sample duplicates. Otherwise hand calculation would be necessary. See Appendix C.

5.3. Blanks- Prepare as follows:

5.3.1. Lab Reagent Blank also known as a Preparation Blank (PBK)– This is reagent water that is treated exactly like a sample, including exposure to all glassware, plastic ware, equipment, digestion and reagents that are used on samples. To prepare, fill an approved metals sample container with Type I D.I. H_2O and add 2 ml. concentrated HNO_3 acid, mix thoroughly, and let stand 16 hr. and check the pH before further processing. Prepare one Preparation Blank for every 20 samples and put it through the entire digestion process.

5.3.2. Calibration Blank – This is Type I reagent water acidified such that the acid concentration and reagent matrix are identical to that of the calibration standards and samples. The software details two calibration blanks;

5.3.2.1. Initial calibration blanks (ICB) – those that immediately follow the initial calibration verification.

5.3.2.2. Continuing calibration blanks (CCB) – those that follow continuing calibration verifications.

5.4. Other quality controls

5.4.3. Lab Fortified Blanks (LFBs)

5.4.3.1. LFB - This is an aliquot of the Lab Reagent Blank that is spiked with a known quantity of analyte prior to digestion. The resulting spike concentration should be > 10X the MDL, but < the midpoint concentration of the calibration curve. Run 1 per 20 samples. Its purpose is to determine whether the method is in control and within accepted control limits of 85 – 115%. If recovery is outside of these limits, source of problem should be identified and resolved before continuing.

5.4.3.2. LFB-MRL - This is an aliquot of the Lab Reagent Blank that is spiked with a known quantity of analyte prior to digestion. The resulting spike concentration is at the reporting limit. Its purpose is to demonstrate that the instrument can detect the concentration of the lowest calibration standard when digested. Accepted control limits are 70-130 %. If recovery is outside of these limits, source of problem should be identified and resolved before continuing.

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5.4.4. Sample Matrix Spike- (MSK) - This is an aliquot of unknown sample matrix to which a known quantity of analyte is added prior to digestion at the same concentration as the LFB. 10% of the samples are spiked or one per batch, whichever is greater. Add the same amount of working standard Hg solution as preparing the LFB to a duplicate sample aliquot in a plastic digestion tube. It is digested and analyzed exactly like a sample to determine whether the sample matrix and/or preparation method contributes bias to results. Recovery should be between 70-130%. If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery problem of the fortified sample is judged to be matrix related, not system related. The result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix effects. All matrix spikes are done in duplicate (MDUP).

5.4.5. Fortified Reagent Water (FRW) – this sample is essentially like the LFB but is made up with lower concentrations of analytes. It is used to determine the Method Detection Limit as discussed in section 5.1.3. After the analyst determines the Instrument Detection Limit (IDL), which is equal to three times the standard deviation of a series of ten replicate measurements of a calibration blank, an FRW sample is made up. To a one liter flask of Type I H_20, add levels of analyte to equal 2 – 3 times the IDL concentration. Add 2 ml conc. HNO_3, store in plastic sample bottle for at least 16 hr. before further processing.

5.4.6. Laboratory Duplicate (LDP) - This is a preparation duplicate of a sample that is taken through entire digestion process used determine if the digestion process affects precision. Comparison of results and action discussed can be found in appendix A.

5.4.7. Minimum Reporting Limit (MRL) - This is a LFB that matches the concentration of the lowest standard of the calibration curve. Accepted control limits are 70-130%.

5.4.8. Calibration Verifications 5.0 ppb (CVs) – The method calls this an Instrument Performance Check. This is an intermediate concentration calibration standard analyzed immediately after the initial calibration, after every 10 analyses, and at the end of the run that validates the calibration and stability of the instrument. The concentration is 50% of the highest calibration standard used.

5.4.8.1. Initial Calibration Verification (ICV) - immediately following the calibration- acceptance limits are +/- 5% recovery.

5.4.8.2. Continuing Calibration Verification (CCV) – subsequent calibration checks - acceptance limits are +/- 10% recovery.

5.4.9. Laboratory Control Sample (LCS) – This is a second source standard, one not used to calibrate the instrument, which is used to confirm the validity of the calibration and calibration standards. The acceptance limits are ± 10%.

5.5. Records- The dates of preparation and initials of analyst must be recorded in the logbook for all blanks, standards, and quality controls discussed in section 5. Lot numbers must be documented for all solutions and reagents.

6. Procedure and Data Analysis

6.1 Initial Instrument Set-up

6.1.1. Secure the peristaltic pump tubes on to the pump as described in the instrument

manual. Replace if tubes are worn or don't deliver an even flow.

6.1.2. Disconnect the black tubing going to the Nafion dryer from the gas liquid separator (GLS)

6.1.3. Open the regulator on the Argon cylinder and adjust the pressure to 60 psi, to aid in wetting of the GLS center post. Note this is optional and not necessary.

6.1.4. Power up the computer, printer, monitor, instrument, autosampler, and peristaltic pump.

6.1.5. Select the QuickTrace icon on the computer desktop to initialize the software, pumps, and mercury lamp

6.1.6. Allow at least 15 minutes for the mercury lamp to warm up.

6.1.7. Allow the center post of the GLS to become wet and reconnect the tubing going to the Nafion dryer **after** the GLS has drained.

6.1.8. Re-adjust the pressure regulator to 40 psi., check flowmeter and make adjustments with the metering valve to obtain a flow of 125 ml/min.

6.2 Instrument Sequence Set-up

6.2.1. Goto **File**, at the top of the page, scroll down and select, **New from**, and then select **Template**. The template worksheet is used to download instrument conditions and sequence information according to the concentration range desired for analysis.

6.2.2. From the list of template worksheets, select **Hg 0.2-10.0 ppb**.

6.2.3. Under template name enter the batch label to be used, for example, 091206a, would indicate month, date, year, and batch. 09/12/06 batch a. Another system of nomenclature is acceptable as long as it is explained and consistent. Integration with a LIMS system may require a different nomenclature than stated above. This is undetermined at this time and is pending.

6.2.4. To store data electronically, goto **window** at the top of the page and scroll down to **sequence parameters** and select **reports**. In report dialog box enter the file name and location where data is to be stored. For example C:\Hg_Data\09_06_Data\batch number (see 6.2.3. - 091206a)

6.2.5. Goto **window** at the top of the page and scroll down and select **sequence editor**.

6.2.6. Click the sequence box and enter the total number of samples to be run in the designated box, add more than is needed. They can be removed at a later time. Then select **Generate Sequence** at the bottom of the page. This will produce a sequence listing that begins with the predetermined calibration standards, initial quality control samples, and a sample listing that can be edited with the appropriate sample numbers, autosampler position and sample types. If more or less samples are needed goto **edit** at the top of the page and make the appropriate selection according to what is needed for the day of analysis.

6.2.7. On the sequence table page enter the sample labels/ numbers according to the tube position on the autosampler. For example, tube position **1:5** indicates rack **one**, position **five**.

6.2.8. Enter sample type, this will tell the software whether the sample is a quality control or an unknown. Sample types in the software differ slightly from those listed in the method but their meaning is the same.

6.2.9. Once sequence information has been entered on the sequence page, right click the

mouse, scroll down and select **print sequence**.

6.2.10. Set the instrument up so that it will go into stand-by mode after sequence is done by selecting **window** from the top tool bar. Scroll down and select **sequence parameters**. On the page that opens, check the box that says **pump** and select **off**. Select **file** from the top of the page and select **save**.

6.2.11. Load autosampler according to how it was entered into the sequence page.

6.2.12. Place the reagent sipper tube into the 10% $SnCl_2 \cdot H_2O$ solution.

6.2.13. Prior to calibrating the instrument, set the read times for the baseline drift and analyte peak by analyzing the 2 ppb Hg standard. To do this, select the **Analyze single sample** icon from the top tool bar. Enter the requested information and select **OK**. The analyzer will now read this preliminary sample. Observe and make note of the read time for the baseline and analyte peak. Goto **Method Editor** and make the necessary adjustments to these read times, then save this to the method. This will allow the instrument to compensate for daily variations of room temperature and pressure.

6.2.14. Select **Go** at the top of the page to start analysis.

6.2.15. Reports will be generated automatically at the end of the run.

6.2.16. **Note**: all the program conditions have been previously determined so that every time this worksheet (Hg 0.2- 10.0 ppb) is retrieved, the same instrument parameters will be used for analysis. **Important** - do not change the instrument parameters. If new parameters are desired then create a new method according to the analytical and detection limit needs.

6.3. Instrument shut down procedure

6.3.1. Remove the reagent sipper tube from the 10% $SnCl_2 \cdot H_2O$ solution, and place it into a container with 1%HNO_3/HCL. Allow this solution to flush out the pump tubes and GLS for several minutes. Upon completion remove the sipper tube and allow the pump tubes to completely empty.

6.3.2. Exit the QuickTrace software by selecting **X** at the top right hand corner of the page.

6.3.3. Release the tensioning clamps on the peristaltic pump, and remove the pump tubes from the tubing bridge.

6.3.4. Turn off the computer, and power supply transformers to the autosampler, analyzer, and peristaltic pump.

6.4 Methodology- Use only EPA approved methods for drinking water.

6.4.1 Approved Methods- EPA Method 245.1 "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. " Revision 3.0. May 1994

a. Modifications to method:

(1.) Use reagents as specified in this Standard Operating Procedure.

(2.) Use digestion procedure as described in this Standard Operating Procedure.

(3.) The Correlation Coefficient will automatically be calculated, if greater than or equal to 0.995 continue analysis, if less than 0.995 stop and correct problem and recalibrate.

(4.) Run matrix spikes (MSK) in duplicate (MDUP) on every 10 samples or 1 per batch. Recovery should be between 70-130%. If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery

problem of the fortified sample is judged to be matrix related, not system related. The result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix effects. All samples are spiked duplicate. Calculate the RPD between duplicates. RPD must be <20%

(5.) LCS limits are +/-10% of true value. If outside limits, stop analysis and correct problem and document before repeating and continuing.

(6.) Run LRB. For each batch, or 1 per 20 samples, LRB should be less than MDL (See 5.3.1). LRB values that exceed the MDL indicate lab or reagent contamination. When LRB values are ≥ 10% of the analyte level determined for a sample or is 2.2 times the MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again after the source of contamination has been corrected and acceptable LRB values have been achieved.

(7.) Run a MRL for each batch, check against limits of +/- 30%. If above or below recovery limits, repeat analysis. If 2nd analysis is still outside limits, suspect poor precision, or analyte loss or contamination during preparation, consider raising lower limit of calibration curve, or investigate and correct.

(8.) Run both types of LFBs once per batch, or 1 per 20 samples. Calculate as percent recovery using the following equation:

$$R = [(LFB)/S] \times 100$$

Where: R= percent recovery

LFB= lab fortified blank, or LFB-MRL

S= concentrated equivalent of analyte added to fortify LRB solution.

The recovery limits are as follows:

LFB - control limits of 85-115%. If outside of limits, investigate and correct problem.

LFB-MRL - control limits of 70-130%. If outside of limits, investigate and correct problem.

7. Maintenance

7.1. Cleaning absorption cell windows- quartz windows need to be cleaned only when the Nafion dryer has been flooded and should be cleaned with 2-propanol as described in the operator's manual. Follow the manual for more specific directions.

7.2. Maintenance Log- Instrument Log is to be kept up to date. Record in detail any work done. Also record in detail any problems that occur during usage.

7.3. Service Contract- If service contract is maintained as recommended by EPA, keep on file for reference to determine coverage, etc.

7.4. **Important** - Thoroughly rinse analyzer's components of $SnCl_2$ by placing the sipper tube into a solution of 5% HCl and allowing the system to flush for 5- 10 minutes. Follow up with a DI water rinse.

7.5. Replace Nafion dryer and pump tubing as needed

7.6. Replace mercury lamp as needed.

7.7. Refresh the $KMnO_4$ in the scrubber when its color changes from purple to brown indicating the permanganate has oxidized.

7.8. Consult the instrument operator's manual for more detailed maintenance information.

8. Safety Precautions:

8.1. The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized.

8.2. Mercury compounds are highly toxic if swallowed, inhaled or absorbed through the skin

8.3. Wear protective clothing, eye protection, and gloves when handling acids, standards, reagents, and samples.

8.4. Store Acid in the Acid cabinet.

8.5. Report all accidents and spills to the lab supervisor, use spill clean up kits located in metals prep room.

8.6. Clean up broken glass immediately and discard in proper container.

8.7. Store expired standards and reagents safely until a contractor can pick them up for disposal.

8.8. The compressed Argon gas cylinder must be strapped and immobile using the strap clamp attached to the desk.

9. References:

9.1. EPA Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA-600/R-94-111, May 1994.

9.2 EPA Manual for the Certification of Laboratories Analyzing Drinking Water, fifth edition, EPA 815-R-05-004, January 2005.

9.3 Standard Methods, 18th Edition, Method SM3112B, 1992

9.4 40 CFR Part 136 Appendix B

9.5 Cetac QuickTrace M-6100 Mercury Analyzer Operator Manual, Version 1.0.1

9.6 Cetac QuickTrace Mercury Analyzer Software Manual

Appendix A

Quality Control Limits And Corrective Action Summary For EPA 245.1

Calibration Verifications 5.0 PPB

LIMITS: Initial (ICV) ± 5.0 %

Continuing (CCV) ± 10.0 %

Corrective Action: Repeat: Upon second failure, cease analysis, recalibrate, repeat CCV or ICV Standard; reanalyze all samples back to last acceptable CCV.

Calibration Blanks (ICB & CCB) LIMITS: <MDL

Corrective Action: Repeat. Upon second failure, cease analysis, recalibrate, repeat CCV Standard and CCB, reanalyze all samples back to last acceptable CCV/CCB

Laboratory Control Sample (LCS) LIMITS: 90– 110%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause and rectify before continuing analysis.

Preparation Blank (PBK) LIMITS: <MDL, if samples contain Hg, the PBK values must be < 10% of sample analyte value, or < 2.2 times the MDL

Corrective Action: Repeat. Upon second failure, cease analysis, determine source of contamination and eliminate. If found necessary, re-digest sample batch before continuing.

Laboratory Fortified Blanks (LFBs)

LFB – LIMITS: 85-115%

LFB-MRL – LIMIST: 70-130%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause of analyte loss or source of contamination and rectify. If found necessary, re-digest sample batch before continuing.

Minimum Reporting Limit (MRL) LIMITS: 70– 130%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause and rectify before continuing. If MRL fails often, consider raising concentration level of the low standard of the curve and the MRL.

Laboratory Duplicate (DUP) LIMITS: ≤ 20%RPD

Corrective Action: Review sample preparation procedures, correct any observed problems and repeat sample and lab duplicate preparation and analysis

Freedom_0006095_0284

<u>Sample Matrix Spike (MSK and MDUP)</u> LIMITS: 70–130% Recovery, 20% RPDs for spike duplicates

If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery problem of the fortified sample is judged to be matrix related, not system related. The result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix effects.

Document all corrective actions in logbook.

Freedom_0006095_0285

Appendix B

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAY - 8 2001.

OFFICE OF WATER

John Stone
Vice President
Environmental Express, Ltd
490 Wando Park Blvd.
Mt. Pleasant, SC 29464

Dear Mr. Stone:

This letter responds to your letter regarding the use of the Environmental Express HotBlock™ digestion system with EPA methods currently approved or soon to be proposed for the determination of mercury. Specifically your letter referenced EPA Methods 245.1, 245.2, 245.7 (to be proposed), 7470, 7471, and 1631. As stated in an earlier letter, EPA does not approve or endorse specific instrumentation However, provided that all procedures in the approved methods are followed, and all QA/QC criteria are met, the HotBlock™ is acceptable for use as a heating source in methods approved or proposed by EPA's Office of Water for use in National Pollutant Discharge Elimination System (NPDES) or National Primary Drinking Water Regulations (NPDWR) compliance monitoring. These methods include but are not limited to EPA Methods 245.1, 245.2, 245.7 and 1631.

For written clarification regarding the use of the Environmental Express HotBlock™ with EPA Methods 7470 and 7471, or other methods contained EPA's Office of Solid Waste methods manual, *known as Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846)*, you will need to contact EPA's Office of Solid Waste. Written inquiries regarding SW-846 methods may be submitted to the following address: OSW Methods Team, U.S. Environmental Protection Agency Office of Solid Waste (5307W), Ariel Rios Building, 1200 Pennsylvania Ave. NW, Washington, DC 20460. Fax: 703-308-0511.

Alternatively, you may submit an inquiry through the Methods Information Communication Exchange (MICE) Service. The service provides timely answers to method related questions and takes comments on technical issues regarding the EPA Office of Solid Waste methods. The MICE Service can be reached by telephone (703-676-4690), by fax (703-903-1373), or by e-mail: mice@epmx.saic.com.

If I can be of additional assistance on this and other matters, please write or call me at (202) 260 1639 at your convenience.

Sincerely,

Maria Gomez-Taylor

Maria Gomez-Taylor, Ph.D
Analytical Method Staff
Engineering and Analysis Division (4304)

Freedom_0006095_0286

Appendix C
Software Variations from Method Quality Controls and Sample Labels

Note: The purpose of these alternate labels is for automated calculations by the software.

Method Label	Software Label
Instrument Performance Check (IPC)	Initial Calibration Verification (ICV) Continuing Calibration Check(CCV)
Calibration Blank	Initial Calibration Blank (ICB) Continuing Calibration Blank (CCB)
Laboratory Reagent Blank (LRB)	Preparation Blank (PBK)
Quality Control Sample (QCS)	Laboratory Control Sample (LCS)
Laboratory Duplicate (LDP)	Duplicate (DUP)
Lab Fortified Sample Matrix (LFM)	Matrix Spike (MSK)
LFM Duplicate	Matrix Spike Duplicate (MDUP)

Freedom_0006095_0287

Ex. 5 - Deliberative

COPY

Initial Demonstration of Capability
For Precision and Accuracy
Data Summary

Method SM3111B **Analyte** Cu

Quality Control Sample (lot#) J.T. Baker (A36701)

True Value 0.50 ppm

Date QC Sample Made 9-20-06

Date QC Sample Digested 9-22-06

Date of Analysis 9-27-06

Replicate	Concentration mg/L	Percent Recovery
1	0.520	104.0
2	0.520	104.0
3	0.507	101.4
4	0.509	101.8

Mean Recovery 0.514 (102.8%) **Accuracy Limit 100 ± 10%**

% RSD 1.36 **Precision Limit < 5% RSD**

Pat Marshio 9/27/06
Analyst/ Date

9-27-06
Program Manager/Date

Copper
IDC,
MDL

COPY

Varian SpectrAA 300/400 System Report

OPERATOR Pat Marchio pm
DATE Sept 27,2006
BATCH Cu

PROGRAM 10 Cu 0.025-1.000 PPM

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	INTEGRATION
LAMP POSITION	5
LAMP CURRENT (mA)	2
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	324.8
FLAME	AIR-ACETYLENE
SAMPLE INTRODUCTION	MANUAL
DELAY TIME	4
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	4.0
REPLICATES	3
BACKGROUND CORRECTION	ON
AIR FLOW (L/min)	14.3
ACETYLENE FLOW (L/min)	2.00

CONDITIONS FOR Cu

PMV = 307.7

IDL= 0.007 8/25/06
MDL= 0.004 5/6/05
LDR= 4.0PPM 4/27/05

SAMPLE	CONC mg/L	%RSD	MEAN ABS	READINGS			
BLANK	0.000		-0.175	-0.175	-0.176	-0.175	
BLANK	0.000		0.000	0.000	-0.000	0.000	
STANDARD 1	0.025	1.2	0.005	0.005	0.005	0.005	
STANDARD 2	0.050	1.4	0.009	0.009	0.010	0.009	
STANDARD 3	0.100	1.0	0.019	0.019	0.020	0.019	r = 0.9999
STANDARD 4	0.500	1.4	0.094	0.095	0.093	0.096	
STANDARD 5	1.000	0.7	0.184	0.183	0.185	0.183	
QCSTD0.50PPM	0.503	0.3	0.095	0.095	0.095	0.095	%R=100.6
QC BLANK	0.001	99.9	0.000	0.000	-0.000	0.001	< IDL
QCS 0.20 PPM	0.200	0.0	0.039	0.039	0.038	0.039	%R=100.0
LRB 0.025 ppm	-0.001	32.6	-0.000	-0.000	-0.000	-0.000	< MDL
MRL ~~2.00~~ PPM	0.021	3.3	0.004	0.004	0.004	0.004	~~%R=105.0~~ %R=84.0
LFB 0.025PPM	0.023	4.3	0.005	0.005	0.005	0.005	~~%R=115~~ %R=92.0
LFB 0.08 PPM	0.079	2.6	0.015	0.015	0.015	0.016	%R=98.8
QCSTD0.50PPM	0.502	0.7	0.095	0.095	0.095	0.094	%R=100.4
QC BLANK	0.001	99.9	0.000	0.001	-0.000	-0.000	< IDL
IDC-1 .5PPM	0.520	0.4	0.098	0.098	0.098	0.098	%R= ~~105~~ 104.0
IDC-2 .5PPM	0.520	0.5	0.098	0.098	0.098	0.098	%R= 104.0
IDC-3 .5PPM	0.507	0.2	0.096	0.095	0.096	0.096	%R= 101.4
IDC-4 .5PPM	0.509	0.5	0.096	0.095	0.096	0.096	%R= 101.8
							$\bar{x}$ = 0.514; $\overline{\%R}$ = 102.8; %RSD = 1.36
LRB	-0.002	14.6	-0.000	-0.000	-0.000	-0.000	< MDL
LFB 0.025PPM	0.023	2.3	0.005	0.005	0.005	0.005	%R= 92.0
LFB 0.08 PPM	0.076	0.9	0.015	0.015	0.014	0.015	%R= 95.0
QCSTD0.50PPM	0.501	0.2	0.095	0.095	0.095	0.094	%R= 100.2
QC BLANK	-0.003	57.7	-0.001	-0.000	-0.001	-0.001	> -IDL
QCS 0.20 PPM	0.001	98.7	0.000	0.000	-0.000	0.001	mistake Pum
FRW1-1	0.004	21.9	0.001	0.001	0.001	0.001	
FRW1-2	0.003	41.1	0.001	0.001	0.001	0.000	
FRW1-3	0.005	14.1	0.001	0.001	0.001	0.001	
FRW1-4	0.005	16.7	0.001	0.001	0.001	0.001	
FRW1-5	0.006	13.6	0.001	0.001	0.001	0.001	
FRW1-6	0.006	20.5	0.001	0.001	0.001	0.001	
FRW1-7	0.005	67.5	0.001	0.002	0.001	0.000	
							FRW-1 T.U. = 0.007; $\bar{x}$ = 0.00486; S_y = 0.00106; %RSD = 22.0; MDL = 0.003
QCSTD0.50PPM	0.500	0.0	0.094	0.094	0.094	0.094	%R=100.0
QC BLANK	-0.003	54.7	-0.001	-0.000	-0.001	-0.001	> -IDL
FRW2-1	0.008	8.8	0.002	0.001	0.002	0.002	
FRW2-2	0.010	13.8	0.002	0.002	0.002	0.002	
FRW2-3	0.010	13.5	0.002	0.002	0.002	0.002	
FRW2-4	0.009	18.3	0.002	0.001	0.002	0.002	
FRW2-5	0.009	12.9	0.002	0.002	0.002	0.002	
FRW2-6	0.008	16.1	0.002	0.002	0.002	0.001	
							FRW-2 T.U. = 0.014; $\bar{x}$ = 0.0090; S_y = 0.000816; %RSD = 9.07; MDL = 0.002
FRW2-6	0.009	7.1	0.002	0.002	0.002	0.002	
QCSTD0.50PPM	0.511	0.5	0.096	0.096	0.097	0.096	%R=102.2
QC BLANK	-0.005	19.0	-0.001	-0.001	-0.001	-0.001	> -IDL

FRW-2 %RSD < 10%, data not used

Robin Costas/ESC/R3/USEPA/US
09/25/2006 05:08 PM

To patrickmarchio@wvdhhr.org
cc
bcc
Subject mercury questions

Hi there Pat. I wanted to get back to you on your mercury questions. Turns out that using HCl in your SnCl (or SnSO4) soln to keep it clear is a pretty common practice among the EPA labs. Especially since Perkin Elmer came out with their method (see attached.) There is a letter at the end from EPA saying that this is an equivalent method. So take a look at that. I think you can go ahead and start using the HCl. Most everyone is still using nitric in the standards, though, although they agree that both work.

HG 245.1 ENVA-100- 011397 .pdf

Hopefully this is what you needed to know...if not, just ask.
robin

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

***Primary** Contaminants for special monitoring - no MCL (141.41):*
Water system must be analyzed for Na at least once a year and reported to EPA. Must use methods in table 141.23(k)(1).

Parameter	Calibration Standards(mg/L)	MDL(mg/L)	WS 79	WS 91	WS 103	WS 115
Sodium 3111B 200.7	Blk;		P	P	P	P

*Optional **Primary** Contaminants which must be certified if they are to be reported - no MCL (141.23(k)(3)):*
These are to be listed as a primary if they are to be certified.

Parameter	Calibration Standards(mg/L)	MDL(mg/L)	WS 79	WS 91	WS 103	WS 115
Calcium	Blk;		–	–	–	–
Nickel	Blk;		P	P	P	P
Magnesium	Blk;		–	–	–	–
Silica	Blk;		–	–	–	–

***Secondary** Contaminants - primarily affect aesthetic quality unless very high concentrations. Can use any method and they don't need to be certified (Part 143). Report as Acceptable or Not.*
"The regulations are not Federally enforceable but are intended as guidelines for the states." (SMCL table - 143.3.)

Parameter	Calibration Standards(mg/L)	SMCL (mg/L)	WS 115	WS 115 makeup	MDL(mg/L)	WS 79	WS 91	WS 91 makeup	WS 103	WS 103 makeup
Aluminum	Blk;	0.05-0.2	F	P		P	P	F	F	P
Copper *(also a primary)*	Blk;	1.0	F	P		P	P	-	P	-
Iron	Blk;	0.3	P			P	P	-	P	-
Manganese	Blk;	0.05	P			P	P	-	P	-
Silver	Blk;	0.1	P			P	F	P	P	-
Zinc	Blk;	5.0	P			P	P	-	P	-

I:\ASQAB_AT Team\FORMS\METALS\SDWA primary and secondary rules 2.wpd

Title 40 Part 141 and Part 143
SDWA requirements for Certification of Metals
January 2002

***Primary** Contaminants with MCL values (141.62):*
Shall be analyzed to determine compliance with the MCLs listed in 141.62. The MCL for arsenic will become 0.010 mg/L on January 23, 2006. Must use methods in table 141.23(k)(1).

Parameter	Calibration Standards(mg/L)	MCL(mg/L)	MDL(mg/L)*	4-23-03 WS79 PT	S	4-24 2004 WS91 PT	makeup 7.16.04	2005 WS 103	2006 WS115
Antimony (200.8,.9) 3113B	Blk;	0.006		P		P		P	P
Arsenic (200.7,.8,.9) 3113B	Blk;	0.01		P		P		P	P
Barium (200.7,.8) 3111B 3113B	Blk;	2		P		P		P	P
Beryllium (200.7,.8,.9) 3113B	Blk;	0.004		P		F	P	P	P
Cadmium (200.7,.8,.9) 3113B	Blk;	0.005		P		P		P	P
Chromium (200.7,.8,.9) 3113B	Blk;	0.1		P		P		P	P
Mercury (245.1,.2,200.8)	Blk;	0.002		P		P		P	P
Selenium (200.8,.9) 3113B	Blk;	0.05		P		F	P	P	P
Thallium (200.8,9)	Blk;	0.002		P		P		P	P

(*MDL - fill in laboratory values for comparison)

***Primary** Contaminants with PQL levels (141.89):*
*SubPart I of 141 - Lead and Copper Rule - If either Pb or Cu exceeds the Action Level, then water system must implement treatment procedure which includes analyzing **calcium** for hardness and **silica** when a silicate compound has been added to the water. Must use methods in table 141.23(k)(1).*

Parameter	Calibration Standards(mg/L)	AL / PQL(mg/L)*	MDL(mg/L)*	WS79	WS91	WS103	WS115
Copper (200.7,.8,.9) 3113B 3111B	Blk;	1.3 / 0.050		P	P	P	F
Lead (200.8,.9) 3113B	Blk;	0.015 / 0.005		P	P	P	P

Makeup P

*AL = Action Level
*PQL = Practical Quantitation Limit
*Must report values as measured between PQL and MDL or ½ PQL.

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

3.95 mg/L
8.5
wipes

WESTON
MANAGERS DESIGNERS/CONSULTANTS

SHEET ____ of ____

CLIENT/SUBJECT _____ W.O. NO. _____

TASK DESCRIPTION _____ TASK NO. _____

PREPARED BY _____ DEPT _____ DATE _____

MATH CHECK BY _____ DEPT _____ DATE _____

METHOD REV. BY _____ DEPT _____ DATE _____

APPROVED BY _____

DEPT _____ DATE _____

Al PM 8.24.06 MDL 1.0 ppb
3113B

Ba PM 8.31.06 MDL .000503 ppm
200.7

Ba 35ml 350µl 95° 1.0% Nitric .5% HCl 200.7 4.4 STDS

200.7	
Sample	STDS
2%	2%
1%	2%

↓ 7 ↓ 35

LFB 8-115 at 0.2 ppm DO ~~dc~~ dup LFSM? spike dups? ← IN SOP

QC spike?

QC Blank < IDL ?
LRB < MDL ?

3113 18th ED

35ml 1750µl HNO_3 95° 5% vs 5.2%?
↓ 20% (1") ↓ 35

↳ don't need to adjust for preservation or explain - do for ICP?

Alse 35ml 350µl HNO_3 95° 1%
700µl H_2O_2 2%
↓ 50% (17.5ml) ↓ 35

OK 5.4.6

no matching STDS → ~~NOT IN SOP~~

Cr 35 1750µl HNO_3 95° 5% 1%
350µl H_2O_2
↓ 20% ↓ 35

6.5 - still true? annual only

200.7 SOP
- spelling 4.4
- 5.2.4 add volume

RLV ~~not~~ digested not in SOP
• ~~[illegible]~~ bigger acceptance window if justified.

RFW 10-05-003/A-5/85

$$\frac{4\ ppb \times 25\mu l}{10\ ppb} = 8\ \mu l \rightarrow 16$$

20 µl

Dups digest 1 per 20 ?
Spike " 1 per 10

WESTON
MANAGERS DESIGNERS/CONSULTANTS

SHEET ____ of ____

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PREPARED BY _____ DEPT _____ DATE _____

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METHOD REV. BY _____ DEPT _____ DATE _____

APPROVED BY _____

DEPT _____ DATE _____

Ex. 5 - Deliberative

LDRS
Bld. Log

RFW 10-05-003/A-5/85

Ex. 5 - Deliberative

WESTON
MANAGERS DESIGNERS/CONSULTANTS

SHEET ____ of ____

CLIENT/SUBJECT _____ W.O. NO. _____

TASK DESCRIPTION _____ TASK NO. _____

PREPARED BY _____ DEPT _____ DATE _____

MATH CHECK BY _____ DEPT _____ DATE _____

METHOD REV. BY _____ DEPT _____ DATE _____

APPROVED BY _____

DEPT _____ DATE _____

Ex. 5 - Deliberative

WESTON
MANAGERS DESIGNERS/CONSULTANTS

SHEET ____ of ____

CLIENT/SUBJECT _____ W.O. NO. _____

TASK DESCRIPTION _____ TASK NO. _____

PREPARED BY _____ DEPT _____ DATE _____

MATH CHECK BY _____ DEPT _____ DATE _____

METHOD REV. BY _____ DEPT _____ DATE _____

APPROVED BY

DEPT _____ DATE _____

Ex. 5 - Deliberative

SOP # on front page - Per 2 how we it.

RFW 10-05-003/A-5/85

Ex. 5 - Deliberative

WESTON
MANAGERS DESIGNERS/CONSULTANTS

SHEET ____ of ____

CLIENT/SUBJECT _____ W.O. NO. _____

TASK DESCRIPTION _____ TASK NO. _____

PREPARED BY _____ DEPT _____ DATE _____

MATH CHECK BY _____ DEPT _____ DATE _____

METHOD REV. BY _____ DEPT _____ DATE _____

APPROVED BY _____ DEPT _____ DATE _____

Ex. 6 - Personal Privacy

RFW 10-05-003/A-5/85

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 6 - Personal Privacy

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Ex. 5 - Deliberative

Method Detection Limit
Data Summary

Method 245.1 Analyte Hg

Analyst Pat Marchio Intsrument Cetac M6100

True Value of Fortified Reagent Water (FRW)
used 0.050 ppb (FRW-2)

Date.....	Mean of 7 replicates	Standard Deviation	%RSD	MDL
10-23-06	0.04427	0.00226	5.1	0.007
10-25-06	0.02728	0.00188	6.9	0.006
10-27-06	0.01710	0.00210	12.3	0.007

MDL average from 3 non-consecutive days = $0.006\overline{6} = 0.007$ ppb

10-30-06

MDL study
Day 1

CETAC Hg Analysis Report

Analyst: Pat Marchio PLM
Worksheet file: C:\Program Files\QuickTrace\Worksheets\102306c.wsz
Date Started: 10/23/2006 12:45:07 PM
Comment: Baseline drift turned off

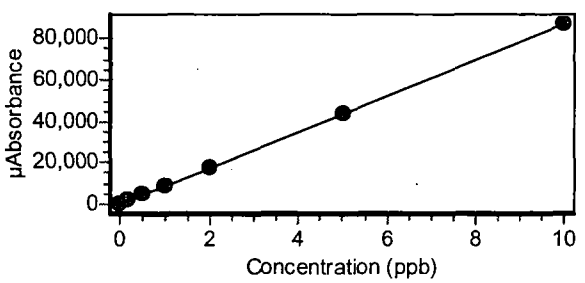
Ex. 5 - Deliberative

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Calibration Blank					STD	10/23/06 12:51:09 pm	0.000000	143	9.70	
Replicates	141.5	132.1	163.2	136.0						
0.2 ppb					STD	10/23/06 12:53:55 pm	0.200000	1853	1.76	
Replicates	1813.5	1840.9	1885.7	1873.7						
0.5 ppb					STD	10/23/06 12:56:42 pm	0.500000	4569	0.96	
Replicates	4514.6	4553.5	4594.1	4613.5						
1.0 ppb					STD	10/23/06 12:59:28 pm	1.000000	8647	0.82	
Replicates	8559.1	8624.3	8678.1	8724.5						
2.0 ppb					STD	10/23/06 01:02:15 pm	2.000000	17895	2.95	
Replicates	17182.6	17820.1	18204.1	18373.4						
5.0 ppb					STD	10/23/06 01:05:03 pm	5.000000	43610	2.37	
Replicates	42213.3	43490.4	44150.7	44586.1						
10.0 ppb					STD	10/23/06 01:07:51 pm	10.000000	87090	1.43	
Replicates	85383.9	86995.6	87740.4	88241.2						

Calibration

Equation: A = 175.056 + 8694.233C
R2: 0.99997
SEE: 183.5348
Flags:



ICV 5.0 ppb					ICV	10/23/06 01:11:48 pm	5.013000	43757	1.49	
Replicates	42906.9	43635.1	44067.3	44418.6						
% Recovery	100.25									

Freedom_0006095_0329

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
ICB					ICB	10/23/06 01:14:34 pm	-0.016200	34	40.67	
Replicates	48.6	16.1	31.7	40.3						
JT Baker 5.0 ppb LCS					LCS	10/23/06 01:17:20 pm	5.015000	43781	0.45	
Replicates	43529.3	43742.4	43860.8	43991.0						
% Recovery	100.31 ✓									
Prep Blank					PBK	10/23/06 01:20:07 pm	0.000230	177	9.11 Q	Limits have yet to be determined
Replicates	191.1	185.5	177.2	154.4						
MRL 0.2 ppb					UNK	10/23/06 01:22:52 pm	0.193500	1857	1.21	%R = 96.8
Replicates	1824.8	1872.9	1872.1	1858.8						
LFB -MRL 0.2 ppb					UNK	10/23/06 01:25:39 pm	0.175400	1700	5.43	%R = 87.7
Replicates	1596.5	1659.9	1732.6	1810.2						
LFB 2.0 ppb					UNK	10/23/06 01:28:26 pm	1.945000	17081	3.08	%R = 97.2
Replicates	16402.9	16954.3	17360.6	17607.5						
CCV 5.0 ppb					CCV	10/23/06 01:31:14 pm	5.110000	44607	1.50	
Replicates	43696.5	44542.2	44975.9	45212.7						
% Recovery	102.21 ✓									
CCB					CCB	10/23/06 01:33:59 pm	0.010250	264	4.32 Q	Limits have yet to be determin
Replicates	254.9	273.2	274.9	253.8						
FRW1-1					UNK	10/23/06 01:36:47 pm	0.018420	335	2.18	
Replicates	326.7	333.1	344.1	337.1						
FRW1-2					UNK	10/23/06 01:39:34 pm	0.023770	382	1.91	
Replicates	381.7	382.7	372.4	390.1						
FRW1-3					UNK	10/23/06 01:42:21 pm	0.021800	365	4.31	
Replicates	341.9	369.3	368.9	378.3						
Single: FRW1-4					UNK	10/23/06 01:54:41 pm	0.025200	394	5.21	
Replicates	375.7	379.1	419.1	402.7						

FRW - 1 T.V. = 0.026 ppb $\bar{x}$ = 0.02661 S_7 = 0.00289 %RSD = 12.2

MDL = 0.0091 ppb

Freedom_0006095_0330

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: FRW1-5					UNK	10/23/06 01:57:52 pm	0.023640	381	0.94	
Replicates	375.3	381.4	382.6	383.1						
Single: FRW1-6					UNK	10/23/06 02:04:01 pm	0.027390	413	3.04	
Replicates	430.2	414.7	406.1	401.6						
Single: FRW1-7					UNK	10/23/06 02:07:45 pm	0.025410	396	2.23	
Replicates	394.3	385.8	396.4	407.2						
Single: CCV 5.0 PPB					CCV	10/23/06 02:11:05 pm	5.000000	43648	3.19	
Replicates	41808.0	43398.3	44386.7	44998.1						
% Recovery	100.00									
Single: CCB					CCB	10/23/06 02:14:18 pm	0.011670	277	5.14	Q Limits have yet to be determined
Replicates	258.6	272.8	283.1	291.6						
Single: FRW2-1					UNK	10/23/06 02:17:40 pm	0.045910	574	3.61	
Replicates	552.4	562.3	583.8	598.3						
Single: FRW2-2					UNK	10/23/06 02:26:48 pm	0.042700	546	3.09	
Replicates	541.5	526.8	567.4	549.6						
Single: FRW2-3					UNK	10/23/06 02:33:13 pm	0.042910	548	0.92	
Replicates	553.2	549.6	541.2	548.6						
Single: FRW2-4					UNK	10/23/06 02:40:42 pm	0.041950	540	1.37	
Replicates	530.6	541.0	548.6	539.0						
Single: FRW2-5					UNK	10/23/06 02:49:54 pm	0.046250	577	3.63	
Replicates	554.6	564.1	593.9	596.1						
Single: FRW2-6					UNK	10/23/06 03:04:06 pm	0.042530	545	3.04	
Replicates	529.7	537.8	568.1	543.8						
Single: FRW2-7					UNK	10/23/06 03:10:49 pm	0.047630	589	2.10	
Replicates	574.5	604.6	589.7	587.8						

FRW-2 $\bar{x}_7 = 0.04427$ $S_7 = 0.00226$ %RSD = 5.10 %

T.V. = 0.050 ppb MDL = 0.0071 ppb

Freedom_0006095_0331

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: CCV 5.0 PPB					CCV	10/23/06 03:14:09 pm	4.894000	42725	3.69	
Replicates	40704.3	42327.9	43557.9	44311.1						
% Recovery	97.88									
Single: CCB					CCB	10/23/06 03:17:21 pm	0.008464	249	5.18	Q
Replicates	244.8	237.0	267.1	245.7						

Notes

IDL 10/19/06 = 0.026 ppb

Freedom_0006095_0332

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0333

PBK

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0000

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0334

MDL study
DAY 2

CETAC Hg Analysis Report

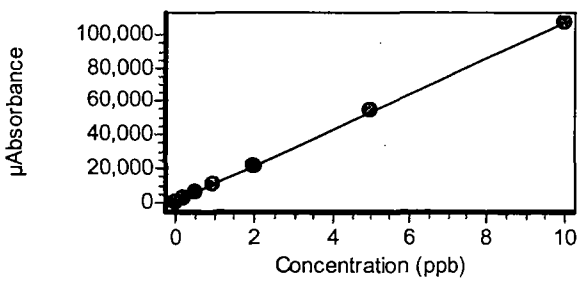
Analyst: Pat Marchio PLM
Worksheet file: C:\Program Files\QuickTrace\Worksheets\102506b.wsz
Date Started: 10/25/2006 10:56:57 AM
Comment: Same conditions as batch 102306c

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Calibration Blank					STD	10/25/06 11:02:24 am	0.000000	245	3.07	
Replicates	241.4	238.4	255.6	244.1						
0.2 ppb					STD	10/25/06 11:05:10 am	0.200000	2394	1.83	
Replicates	2334.1	2390.7	2419.3	2432.8						
0.5 ppb					STD	10/25/06 11:07:56 am	0.500000	5890	1.16	
Replicates	5791.9	5900.4	5947.9	5920.4						
1.0 ppb					STD	10/25/06 11:10:43 am	1.000000	11015	0.16	
Replicates	10988.8	11023.8	11025.2	11021.5						
2.0 ppb					STD	10/25/06 11:13:30 am	2.000000	21880	0.27	
Replicates	21806.5	21858.9	21918.4	21937.6						
5.0 ppb					STD	10/25/06 11:16:18 am	5.000000	54211	0.20	
Replicates	54194.3	54315.4	54270.1	54065.5						
10.0 ppb					STD	10/25/06 11:19:57 am	10.000000	106321	0.15	
Replicates	106149.7	106240.2	106377.8	106518.1						

Calibration

Equation: A = 486.898 + 10617.590C
R2: 0.99993
SEE: 365.7683
Flags:



ICV 5.0 ppb					ICV	10/25/06 11:23:35 am	5.009000	53672	0.17	
Replicates	53793.4	53658.3	53574.6	53659.9						
% Recovery	100.18									

Freedom_0006095_0335

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
ICB					ICB	10/25/06 11:27:11 am	0.008903	581	2.44	Z Limits have yet to be determined
Replicates	565.0	599.0	577.4	584.3						
JT Baker 5.0 ppb LCS					LCS	10/25/06 11:29:57 am	5.152000	55193	0.20	
Replicates	55131.7	55129.5	55156.4	55355.2						
% Recovery	103.05									
Prep Blank					PBK	10/25/06 11:33:34 am	0.024310	745	1.84	Q Limits have yet to be determined
Replicates	747.9	735.0	733.9	763.2						
MRL 0.2 ppb					UNK	10/25/06 11:36:19 am	0.216100	2781	0.48	%R = 108.0
Replicates	2786.5	2782.9	2762.6	2793.4						
LFB -MRL 0.2 ppb					UNK	10/25/06 11:39:06 am	0.217200	2793	0.53	%R = 108.6
Replicates	2792.9	2811.1	2774.9	2791.9						
LFB 2.0 ppb					UNK	10/25/06 11:41:53 am	2.051000	22267	0.15	%R = 102.6
Replicates	22288.4	22301.6	22240.6	22237.8						
CCV 5.0 ppb					CCV	10/25/06 11:44:41 am	5.093000	54567	0.11	
Replicates	54484.7	54582.9	54568.7	54631.6						
% Recovery	101.87									
CCB					CCB	10/25/06 11:48:17 am	0.027210	776	1.13	Q Limits have yet to be determined
Replicates	784.0	781.4	772.9	764.7						
Single: FRW1-1					UNK	10/25/06 11:55:40 am	0.005049	541	1.37	
Replicates	538.5	539.5	533.2	550.9						
Single: FRW1-2					UNK	10/25/06 11:58:52 am	0.007959	571	2.17	
Replicates	587.5	569.2	557.4	571.4						
Single: FRW1-3					UNK	10/25/06 12:02:01 pm	0.004844	538	2.03	
Replicates	527.8	551.5	543.0	531.0						
Single: FRW1-4					UNK	10/25/06 12:05:51 pm	0.003329	522	1.33	
Replicates	516.5	530.0	526.2	516.2						

FRW-1 T.V. = 0.026 ppb $\bar{x}_7$ = 0.005562 S_7 = 0.001776

%RSD = 31.9 MDL = 0.0055 = 0.006 ppb

Freedom_0006095_0336

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: FRW1-5					UNK	10/25/06 12:09:44 pm	0.005344	544	1.46	
Replicates	545.4	554.1	536.8	538.2						
Single: FRW1-6					UNK	10/25/06 12:12:52 pm	0.008014	572	2.08	
Replicates	575.6	554.4	577.5	580.4						
Single: FRW1-7					UNK	10/25/06 12:16:03 pm	0.004392	534	3.48	
Replicates	555.3	534.4	534.6	509.9						
Single: CCV 5.0 PPB					CCV	10/25/06 12:19:28 pm	5.106000	54698	0.11	
Replicates	54620.6	54675.6	54754.6	54742.1						
% Recovery	102.12									
Single: CCB					CCB	10/25/06 12:23:38 pm	-0.023720	235	9.40	Limits have yet to be determined
Replicates	237.9	249.3	203.0	250.1						
Single: FRW2-1					UNK	10/25/06 01:08:03 pm	0.029190	797	1.03	
Replicates	789.5	807.3	799.5	791.0						
Single: FRW2-2					UNK	10/25/06 01:11:34 pm	0.029170	797	2.87	
Replicates	811.7	812.9	763.9	797.9						
Single: FRW2-3					UNK	10/25/06 01:18:14 pm	0.027650	780	1.80	
Replicates	801.1	777.3	772.1	771.4						
Single: FRW2-4					UNK	10/25/06 01:21:33 pm	0.027280	777	2.08	
Replicates	755.6	785.6	792.4	772.6						
Single: FRW2-5					UNK	10/25/06 01:26:37 pm	0.024380	746	2.49	
Replicates	735.9	744.2	772.3	730.6						
Single: FRW2-6					UNK	10/25/06 01:30:28 pm	0.025130	754	1.19	
Replicates	742.3	751.1	762.1	759.5						
Single: FRW2-7					UNK	10/25/06 01:41:41 pm	0.028180	786	2.05	
Replicates	781.9	807.9	769.1	785.5						

FRW-2 T.V. = ~~0.02~~ 0.050 ppb $\bar{X}_7$ = 0.02728 S_7 = 0.001879

%RSD = 6.89 MDL = 0.006 ppb

Freedom_0006095_0337

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: CCV 5.0 PPB					CCV	10/25/06 01:45:08 pm	5.154000	55211	0.09	
Replicates	55141.1	55228.1	55248.1	55226.8						
% Recovery	103.08 ✓									
Single: CCB					CCB	10/25/06 01:50:03 pm	-0.022920	244	8.50	Limits have yet to be determined
Replicates	260.9	233.9	219.0	260.5						

Notes

IDL 10/19/06 = 0.026 ppb

Freedom_0006095_0338

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0339

PBK

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0000

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0340

CETAC Hg Analysis Report

MDL study DAY 3
IDC
LDR

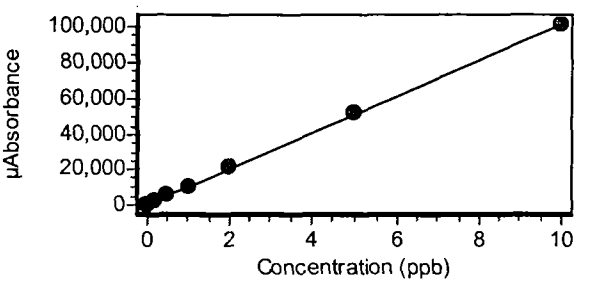
Analyst: Pat Marchio PM
Worksheet file: C:\Program Files\QuickTrace\Worksheets\102706b.wsz
Date Started: 10/27/2006 1:14:04 PM
Comment:

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Calibration Blank					STD	10/27/06 01:18:07 pm	0.000000	219	7.91	
Replicates	241.1	221.9	201.2	209.9						
0.2 ppb					STD	10/27/06 01:20:52 pm	0.200000	2226	0.43	
Replicates	2230.9	2222.6	2236.6	2214.5						
0.5 ppb					STD	10/27/06 01:23:39 pm	0.500000	5539	0.30	
Replicates	5519.9	5539.9	5537.1	5560.7						
1.0 ppb					STD	10/27/06 01:26:25 pm	1.000000	10478	0.25	
Replicates	10454.0	10462.6	10480.3	10514.3						
2.0 ppb					STD	10/27/06 01:29:13 pm	2.000000	21682	0.07	
Replicates	21702.5	21688.1	21671.5	21667.4						
5.0 ppb					STD	10/27/06 01:32:00 pm	5.000000	51435	0.20	
Replicates	51303.9	51516.9	51516.2	51403.7						
10.0 ppb					STD	10/27/06 01:35:40 pm	10.000000	100864	0.11	
Replicates	100804.4	100971.9	100933.5	100745.0						

Calibration

Equation: A = 597.042 + 10067.590C
R2: 0.99980
SEE: 575.2796
Flags:



Single: ICV (5.0 ppb)					ICV	10/27/06 01:39:06 pm	5.053000	51464	0.11
Replicates	51400.6	51497.0	51527.2	51430.5					
% Recovery	101.05								

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: ICB					ICB	10/27/06 01:42:41 pm	-0.037960	215	9.90	
Replicates	237.8	210.6	223.4	187.6						
Single: LCS 5.0 ppb					LCS	10/27/06 01:51:13 pm	4.984000	50773	0.04	
Replicates	50747.5	50781.3	50771.3	50791.3						
% Recovery	99.68									
Single: Perp Blank					PBK	10/27/06 01:54:56 pm	-0.028070	314	2.57	
Replicates	308.6	316.4	325.0	307.6						
Single: MRL 0.2 ppb					UNK	10/27/06 01:58:21 pm	0.168400	2292	0.34	%R= 84.2
Replicates	2283.0	2292.9	2302.1	2290.5						
Single: LFB-MRL 0.2 ppb					UNK	10/27/06 02:01:55 pm	0.188200	2492	0.19	%R= 94.1
Replicates	2489.3	2486.1	2495.0	2495.9						
Single: LFB 2.0 ppb					UNK	10/27/06 02:05:22 pm	2.029000	21021	0.08	%R= 101.4
Replicates	21042.1	21020.6	21004.4	21015.6						
Single: CCV 5.0 ppb					CCV	10/27/06 02:08:55 pm	5.107000	52011	0.31	
Replicates	51774.9	52037.8	52101.6	52127.9						
% Recovery	102.14									
Single: CCB					CCB	10/27/06 02:15:05 pm	-0.037320	221	5.26	
Replicates	207.0	229.1	216.9	232.4						
Single: FRW1-1					UNK	10/27/06 02:18:10 pm	-0.005790	539	2.82	Can not use negative numbers. continue with FRW-2
Replicates	543.9	548.6	516.1	546.4						
Single: FRW1-1 repeated					UNK	10/27/06 02:24:18 pm	-0.008101	515	3.54	
Replicates	525.1	488.3	526.8	521.7						
Single: FRW2-1					UNK	10/27/06 02:27:54 pm	0.019590	794	1.64	
Replicates	793.9	812.8	783.9	786.7						
Single: FRW2-2					UNK	10/27/06 02:31:28 pm	0.018640	785	2.29	
Replicates	789.2	758.4	798.1	793.2						

Freedom_0006095_0342

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: FRW2-3					UNK	10/27/06 02:34:33 pm	0.014340	741	2.77	
Replicates	743.5	760.9	748.6	712.6						
Single: FRW2-4					UNK	10/27/06 02:37:43 pm	0.018950	788	1.78	
Replicates	781.7	774.8	787.6	807.4						
Single: FRW2-5					UNK	10/27/06 02:40:55 pm	0.014490	743	1.99	
Replicates	749.3	750.2	751.4	720.9						
Single: FRW2-6					UNK	10/27/06 02:44:24 pm	0.016870	767	2.01	
Replicates	755.3	781.2	751.9	779.0						
Single: FRW2-7					UNK	10/27/06 02:47:31 pm	0.016820	766	1.62	
Replicates	762.1	777.6	750.9	775.1						
Single: CCV 5.0 ppb					CCV	10/27/06 02:51:44 pm	5.166000	52610	0.32	
Replicates	52371.5	52609.1	52713.5	52744.6						
% Recovery	103.33									
Single: CCB					CCB	10/27/06 02:56:50 pm	-0.035550	239	1.72	
Replicates	244.7	234.8	238.3	238.9						
Single: Prep Blank					PBK	10/27/06 03:02:28 pm	-0.036690	228	1.77	
Replicates	230.5	231.6	224.7	223.6						
Single: LFB-MRL 0.2 ppb					UNK	10/27/06 03:05:39 pm	0.183500	2445	0.60	%R = 91.8
Replicates	2452.5	2426.8	2439.1	2460.1						
Single: LFB 2.0 ppb					UNK	10/27/06 03:09:08 pm	2.042000	21152	0.08	%R = 102.1
Replicates	21128.5	21156.3	21163.8	21160.4						
Single: IDC 2.0 ppb					UNK	10/27/06 03:12:27 pm	1.911000	19841	0.27	%R = 95.6
Replicates	19774.5	19822.6	19881.5	19884.9						
Single: IDC #2 2.0 ppb					UNK	10/27/06 03:16:17 pm	1.930000	20028	0.09	%R = 96.5
Replicates	20024.5	20051.6	20010.6	20026.4						

FRW-2 $x_7 = 0.0171$ $S_7 = 0.00210$

%RSD = 12.3 MDL = 0.0066 = 0.007 mg/l

Freedom_0006095_0343

Sample Name	Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: IDC #3 2.0 ppb	UNK	10/27/06 03:19:44 pm	1.914000	19866	0.16	%R = 95.7
Replicates 19818.3 19875.5 19889.1 19882.4						
Single: IDC #4 2.0 ppb	UNK	10/27/06 03:28:26 pm	1.834000	19065	0.45	%R = 91.7
Replicates 18959.5 19038.9 19100.2 19161.1						
Single: CCV 5.0 ppb	CCV	10/27/06 03:32:08 pm	5.150000	52441	0.18	
Replicates 52330.3 52539.4 52495.2 52397.9						
% Recovery 102.99						
Single: CCB	CCB	10/27/06 03:37:37 pm	-0.036000	235	3.47	
Replicates 235.6 243.9 224.1 234.6						
Single: LDR 20.0 ppb	UNK	10/27/06 03:42:25 pm	O/R	190737	0.21 O	%R = 94.4
Replicates 191158.1 190947.2 190584.6 190257.5			x_i = 18.89 ppb			
Single: LDR 25.0 ppb	UNK	10/27/06 03:47:28 pm	O/R	257356	0.29 O	
Replicates 256369.1 257233.9 257769.7 258049.4			x_i = 25.50			%R = 102.0
Single: LDR 30.0 ppb	UNK	10/27/06 03:54:10 pm	O/R	296239	2.12 O	%R = 97.9
Replicates 303832.3 298607.4 292931.2 289586.6			x_i = 29.37			
Single: LDR 35.0 ppb	UNK	10/27/06 03:59:46 pm	O/R	335771	0.14 O	%R = 95.1
Replicates 336262.7 336094.3 335473.6 335253.7			x_i = 33.29			
Single: LDR 40.0 ppb	UNK	10/27/06 04:05:55 pm	O/R	355773	0.21 O	%R = 88.0
Replicates 356529.5 356089.3 355702.2 354771.2			x_i = 35.28			
Single: CCV 5.0 ppb	CCV	10/27/06 04:12:48 pm	5.168000	52624	0.28	
Replicates 52410.3 52659.4 52729.2 52698.9						
% Recovery 103.36						
Single: CCB	CCB	10/27/06 04:16:15 pm	-0.037680	218	2.69	
Replicates 226.2 216.3 215.3 212.9						

IDC %RSD = 2.26

Notes

IDL 10/19/06 = 0.026 ppb

Freedom_0006095_0344

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0345

PBK

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0000

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0346

Initial Demonstration of Capability
For Precision and Accuracy
Data Summary

Method 245.1 **Analyte** Hg

Quality Control Sample (lot#) J.T. Baker (B13435)

True Value 2.0 µg/l

Date QC Sample Made 10-26-06

Date QC Sample Digested 10-27-06

Date of Analysis 10-27-06

Replicate	Concentration µg/L	Percent Recovery
1	1.911	95.6
2	1.930	96.5
3	1.914	95.7
4	1.834	91.7

Mean Recovery 1.897 **Accuracy Limit** 100 ± 10%

% RSD 2.26 **Precision Limit** < 5% RSD

Pat Marchis 10/27/06
Analyst/ Date

10-30-06
Program Manager/ Date

CETAC Hg Analysis Report

MDL study DAY 3
IDC
LDR

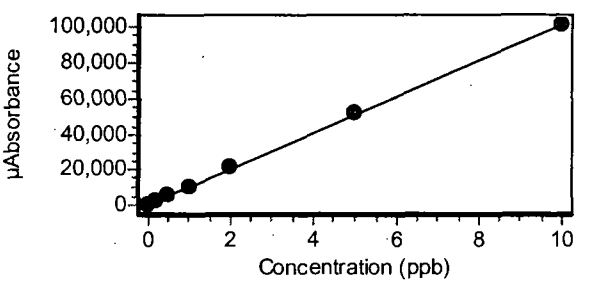
Analyst: Pat Marchio PM
Worksheet file: C:\Program Files\QuickTrace\Worksheets\102706b.wsz
Date Started: 10/27/2006 1:14:04 PM
Comment:

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Calibration Blank					STD	10/27/06 01:18:07 pm	0.000000	219	7.91	
Replicates	241.1	221.9	201.2	209.9						
0.2 ppb					STD	10/27/06 01:20:52 pm	0.200000	2226	0.43	
Replicates	2230.9	2222.6	2236.6	2214.5						
0.5 ppb					STD	10/27/06 01:23:39 pm	0.500000	5539	0.30	
Replicates	5519.9	5539.9	5537.1	5560.7						
1.0 ppb					STD	10/27/06 01:26:25 pm	1.000000	10478	0.25	
Replicates	10454.0	10462.6	10480.3	10514.3						
2.0 ppb					STD	10/27/06 01:29:13 pm	2.000000	21682	0.07	
Replicates	21702.5	21688.1	21671.5	21667.4						
5.0 ppb					STD	10/27/06 01:32:00 pm	5.000000	51435	0.20	
Replicates	51303.9	51516.9	51516.2	51403.7						
10.0 ppb					STD	10/27/06 01:35:40 pm	10.000000	100864	0.11	
Replicates	100804.4	100971.9	100933.5	100745.0						

Calibration

Equation: A = 597.042 + 10067.590C
R2: 0.99980
SEE: 575.2796
Flags:



Single: ICV (5.0 ppb)					ICV	10/27/06 01:39:06 pm	5.053000	51464	0.11	
Replicates	51400.6	51497.0	51527.2	51430.5						
% Recovery	101.05									

Freedom_0006095_0348

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: ICB					ICB	10/27/06 01:42:41 pm	-0.037960	215	9.90	
Replicates	237.8	210.6	223.4	187.6						
Single: LCS 5.0 ppb					LCS	10/27/06 01:51:13 pm	4.984000	50773	0.04	
Replicates	50747.5	50781.3	50771.3	50791.3						
% Recovery	99.68									
Single: Perp Blank					PBK	10/27/06 01:54:56 pm	-0.028070	314	2.57	
Replicates	308.6	316.4	325.0	307.6						
Single: MRL 0.2 ppb					UNK	10/27/06 01:58:21 pm	0.168400	2292	0.34	%R= 84.2
Replicates	2283.0	2292.9	2302.1	2290.5						
Single: LFB-MRL 0.2 ppb					UNK	10/27/06 02:01:55 pm	0.188200	2492	0.19	%R= 94.1
Replicates	2489.3	2486.1	2495.0	2495.9						
Single: LFB 2.0 ppb					UNK	10/27/06 02:05:22 pm	2.029000	21021	0.08	%R= 101.4
Replicates	21042.1	21020.6	21004.4	21015.6						
Single: CCV 5.0 ppb					CCV	10/27/06 02:08:55 pm	5.107000	52011	0.31	
Replicates	51774.9	52037.8	52101.6	52127.9						
% Recovery	102.14									
Single: CCB					CCB	10/27/06 02:15:05 pm	-0.037320	221	5.26	
Replicates	207.0	229.1	216.9	232.4						
Single: FRW1-1					UNK	10/27/06 02:18:10 pm	-0.005790	539	2.82	Can not use negative numbers. continue with FRW-2
Replicates	543.9	548.6	516.1	546.4						
Single: FRW1-1 repeated					UNK	10/27/06 02:24:18 pm	-0.008101	515	3.54	
Replicates	525.1	488.3	526.8	521.7						
Single: FRW2-1					UNK	10/27/06 02:27:54 pm	0.019590	794	1.64	
Replicates	793.9	812.8	783.9	786.7						
Single: FRW2-2					UNK	10/27/06 02:31:28 pm	0.018640	785	2.29	
Replicates	789.2	758.4	798.1	793.2						

Freedom_0006095_0349

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: FRW2-3					UNK	10/27/06 02:34:33 pm	0.014340	741	2.77	
Replicates	743.5	760.9	748.6	712.6						
Single: FRW2-4					UNK	10/27/06 02:37:43 pm	0.018950	788	1.78	
Replicates	781.7	774.8	787.6	807.4						
Single: FRW2-5					UNK	10/27/06 02:40:55 pm	0.014490	743	1.99	
Replicates	749.3	750.2	751.4	720.9						
Single: FRW2-6					UNK	10/27/06 02:44:24 pm	0.016870	767	2.01	
Replicates	755.3	781.2	751.9	779.0						
Single: FRW2-7					UNK	10/27/06 02:47:31 pm	0.016820	766	1.62	
Replicates	762.1	777.6	750.9	775.1						
Single: CCV 5.0 ppb					CCV	10/27/06 02:51:44 pm	5.166000	52610	0.32	
Replicates	52371.5	52609.1	52713.5	52744.6						
% Recovery	103.33									
Single: CCB					CCB	10/27/06 02:56:50 pm	-0.035550	239	1.72	
Replicates	244.7	234.8	238.3	238.9						
Single: Prep Blank					PBK	10/27/06 03:02:28 pm	-0.036690	228	1.77	
Replicates	230.5	231.6	224.7	223.6						
Single: LFB-MRL 0.2 ppb					UNK	10/27/06 03:05:39 pm	0.183500	2445	0.60	%R = 91.8
Replicates	2452.5	2426.8	2439.1	2460.1						
Single: LFB 2.0 ppb					UNK	10/27/06 03:09:08 pm	2.042000	21152	0.08	%R = 102.1
Replicates	21128.5	21156.3	21163.8	21160.4						
Single: IDC 2.0 ppb					UNK	10/27/06 03:12:27 pm	1.911000	19841	0.27	%R = 95.6
Replicates	19774.5	19822.6	19881.5	19884.9						
Single: IDC #2 2.0 ppb					UNK	10/27/06 03:16:17 pm	1.930000	20028	0.09	%R = 96.5
Replicates	20024.5	20051.6	20010.6	20026.4						

FRW-2 $x_7 = 0.0171$ $S_7 = 0.00210$

%RSD = 12.3 MDL = 0.0066 = 0.007 mg/l

Freedom_0006095_0350

Sample Name	Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Single: IDC #3 2.0 ppb	UNK	10/27/06 03:19:44 pm	1.914000	19866	0.16	%R = 95.7
Replicates 19818.3 19875.5 19889.1 19882.4						
Single: IDC #4 2.0 ppb	UNK	10/27/06 03:28:26 pm	1.834000	19065	0.45	%R = 91.7
Replicates 18959.5 19038.9 19100.2 19161.1						
Single: CCV 5.0 ppb	CCV	10/27/06 03:32:08 pm	5.150000	52441	0.18	
Replicates 52330.3 52539.4 52495.2 52397.9						
% Recovery 102.99						
Single: CCB	CCB	10/27/06 03:37:37 pm	-0.036000	235	3.47	
Replicates 235.6 243.9 224.1 234.6						
Single: LDR 20.0 ppb	UNK	10/27/06 03:42:25 pm	O/R	190737	0.21	O
Replicates 191158.1 190947.2 190584.6 190257.5			x_i = 18.89 ppb			%R = 94.4
Single: LDR 25.0 ppb	UNK	10/27/06 03:47:28 pm	O/R	257356	0.29	O
Replicates 256369.1 257233.9 257769.7 258049.4			x_i = 25.50			%R = 102.0
Single: LDR 30.0 ppb	UNK	10/27/06 03:54:10 pm	O/R	296239	2.12	O
Replicates 303832.3 298607.4 292931.2 289586.6			x_i = 29.37			%R = 97.9
Single: LDR 35.0 ppb	UNK	10/27/06 03:59:46 pm	O/R	335771	0.14	O
Replicates 336262.7 336094.3 335473.6 335253.7			x_i = 33.29			%R = 95.1
Single: LDR 40.0 ppb	UNK	10/27/06 04:05:55 pm	O/R	355773	0.21	O
Replicates 356529.5 356089.3 355702.2 354771.2			x_i = 35.28			%R = 88.0
Single: CCV 5.0 ppb	CCV	10/27/06 04:12:48 pm	5.168000	52624	0.28	
Replicates 52410.3 52659.4 52729.2 52698.9						
% Recovery 103.36						
Single: CCB	CCB	10/27/06 04:16:15 pm	-0.037680	218	2.69	
Replicates 226.2 216.3 215.3 212.9						

IDC %RSD = 2.26

Notes

IDL 10/19/06 = 0.026 ppb

Freedom_0006095_0351

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Racalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0352

PBK

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0000

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0000

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Stop analysis

Freedom_0006095_0353

FIGHT Club

G. Calibration & Detection Information:

Maximum Contaminant Level (MCL) and Method Detection Limit (MDL), Minimum Reporting Limit (MRL)

Inorganic Contaminants (IOCs)	Calibration Standards (mg/L)	MCL (mg/L)	MCL ([redacted])	MRL ([redacted])	MDL ([redacted])
Antimony	BLK; 0.003; 0.006; 0.012	0.006	6	3	1.22 Sb
Arsenic	BLK; 0.002; 0.005; 0.010; 0.020	0.010	10	2	0.62 .38 As
Asbestos	Not Analyzed	7 MFL	?	Not Analyzed	Not Analyzed
Barium	BLK; 0.005; 5.0, 10.0	2.00	2000	5	0.0005 Ba
Beryllium	BLK; 0.0002; 0.0005; 0.001; 002	0.004	4	0.2	0.03 Be
Cadmium	BLK; 0.001; 0.002; 0.004	0.005	5	1	0.10 Cd
Chromium	BLK; 0.001; 0.0025; 0.005; 0.010	0.100	100	1	0.48 Cr
Copper (GFAAS)	BLK; 0.001; 0.0025; 0.005; 0.010	1.3*	1300	1	0.19 Cu
Copper (Flame)	BLK; 0.025; 0.050; 0.1; 0.5; 1.0	1.3*	1300	1 .025	0.004 Cu
Cyanide (free)	BLK; 0.05; 0.1; 0.2; 0.3; 0.4	0.2**	200	50	4
Cyanide (total) *	Not Analyzed	0.2**	200	-	-
Fluoride (IC)	BLK; 0.1; 0.2; 0.50; 1.00; 2.00	4.0	4000	100	17
Fluoride (ISE)	BLK; 0.050; 1.00; 3.00; 5.00	4.0	4000	50	25
Lead	BLK; 0.001; 0.0025; 0.005; 0.010	0.015*	15	1	0.18 .17 Pb
Mercury	.2 .5 1.0 2.0 5.0 10.0 ppb	0.002	.002 2	.2 ppb	.006 ppb Hg
Nickel					
Nitrate (IC)	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	10	10,000	100	7.2
Nitrate (TAA)	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	10	10,000	50	5
Nitrate & Nitrite (total) (TAA)	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	0.05	50	50	3
Nitrite (IC)	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	1	1,000	100	4.6
Nitrite (TAA)	BLK; 0.05; 0.10; 0.25; 0.50; 1.00	1	1,000	50	6

Freedom_0006095_0354

Inorganic Contaminants (IOCs)	Calibration Standards (mg/L)	MCL (mg/L)	MCL ([redacted])	MRL ([redacted])	MDL ([redacted])
Selenium ✓	BLK; 0.002; 0.005; 0.010	0.050	50	2 ✓	0.4 ✓ Se
Sodium ✓	BLK; 2.0; 5.0; 10.0; 15.0; 20.0	20.0+	20,000	2000 ✓	0.07 ✓ Na
Thallium	~~BLK; 0.002; 0.004; 0.008~~	0.002	2		

Required relationship: [MCL>MRL>MDL

* "Action Level"
+ "Reportable Level"

H. Quality Control (QC) Procedures:

The laboratory follows a " Manual of Quality Assurance for Environmental Chemistry Laboratory and Environmental Microbiology Laboratory, (QA Manual, Rev. 2009). This document includes: QA plan and policy statement; laboratory organization; employee job descriptions; list of standard operational procedures; WV certified analyses for drinking water (groups); order form for sample bottles; sampling instructions; sample handling procedures; reporting of results; chain of custody (formal internal tracking is limited to cases which may involve litigation); quality assurance monitoring; analytical procedures; data reduction; data verification; data validation; data reduction, validation, reporting and storage; preventive maintenance; internal quality control and corrective action; precision and accuracy samples; proficiency testing; quantitative verification check with each batch of samples; and acronyms and definition of terms.

A partial list of the QC procedures observed during this inspection included: on-going temperature records of refrigerators and drying ovens; analysis of an external (2nd source) QC sample with each analytical batch; routine digestion and analysis of a blank spiked at the reporting level, method detection limit determinations; duplicate analysis (precision measure); spike analysis (accuracy/recovery measure); blank analysis/batch; check standards (instrument performance checks) at beginning, end and 10% frequency (instrument drift measure); cadmium column reduction efficiency measured and recorded; standard weights employed to verify balance performance; on-going compilation and charting of QC check results; and the resistance/conductivity of lab pure water recorded each day of use.

Analysis of an MRL level spike with each sample set. Verification of electronic temperature monitoring devices quarterly.

I. Analytical Deviations:

Deviations (findings) are those laboratory techniques not in compliance with the mandatory

Freedom_0006095_0355

Attachment #4: Appendix E

REQUIRED ANALYTICAL CAPABILITY FOR PRINCIPAL STATE LABORATORY SYSTEMS

Inorganic Contaminants (IOCs)	Methodology * 40 CFR	Maximum Contaminant Level (MCL) 40 CFR
Antimony	141.23	141.23 & 141.62
Arsenic	141.23	141.23 & 141.62 (141.11 has expired)
Asbestos	141.23	141.23 & 141.62
Barium	141.23	141.23 & 141.62
Beryllium	141.23	141.23 & 141.62
Cadmium	141.23	141.23 & 141.62
Chromium	141.23	141.23 & 141.62
Copper	141.23 & 141.89 & 143.4	TT/AL 141.80 & 143.3
Cyanide (free) **	141.23	141.23 & 141.62
Cyanide (total) ***	141.23	--------
Fluoride	141.23 & 143.4	141.62 & 143.3
Lead	141.23 & 141.89	TT/AL 141.80
Mercury	141.23	141.23 & 141.62
Nickel	141.23	No MCL, must monitor, 141.23
Nitrate	141.23	141.11, 141.23 & 141.62
Nitrate and Nitrite (total)	141.23	141.62
Nitrite	141.23	141.23 & 141.62
Selenium	141.23	141.23 & 141.62
Sodium	141.23	No MCL, must monitor, 141.41
Thallium	141.23	141.23 & 141.62

Radioactive Contaminants	Methodology * 40 CFR	Maximum Contaminant Level (MCL) 40 CFR
Alpha particles (Gross Alpha)	141.25	141.66
Beta particle and photon emitters (Gross Alpha and Beta)	141.25	141.66
Radium 226 and Radium 228 (total)	141.25	141.66
Uranium	141.25	141.66

STATES MAY REQUIRE THE FOLLOWING ANALYTICAL CAPABILITIES FOR PRINCIPAL STATE LABORATORY SYSTEMS

Other Analytical Capability	Methodology * 40 CFR	Reference 40 CFR
Bromide	141.131	141.131
Magnesium	141.23 & 141.131	141.131
Specific Ultraviolet Absorbance (SUVA)	141.131	141.131
Total Organic Carbon (TOC)	141.131	141.131 & 141.135
Turbidity	141.74	141.22 & TT 141.70-74 & TT 141.550-553 &

Corrosion Control Treatment Requirements	Methodology * 40 CFR	Reference 40 CFR
Alkalinity	141.23 & 141.89 & 141.131	141.82 & 141.87 & 141.131 & 141.135
Calcium	141.23 & 141.89	141.82 & 141.87
Conductivity	141.23 & 141.89	141.82 & 141.87
Orthophosphate	141.23 & 141.89	141.82 & 141.87
pH	141.23 & 141.89 & 141.131 & 143.4	141.74 & 141.82 & 141.87 & 141.131 & 143.3
Silica	141.23 & 141.89	141.82 & 141.87
Temperature	141.23 & 141.89	141.74 & 141.82 & 141.87

National Secondary Drinking Water Regulations	Methodology * 40 CFR	Maximum Contaminant Level (MCL) 40 CFR
Aluminum	143.4	143.3
Chloride	143.4	143.3
Color	143.4	143.3
Corrosivity	--------	143.3
Foaming Agents	143.4	143.3
Iron	143.4	143.3
Manganese	143.4	143.3
Odor	143.4	143.3
Silver	143.4	143.3
Sulfate	143.4	143.3
Total Dissolved Solids (TDS)	143.4	143.3
Zinc	143.4	143.3

* Alternate test methods may be listed in Appendix A to Subpart C of Part 141.
** Certified for
*** Screening method.

AL = Action Level
TT = Treatment Technique

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Title 40 Part 141 and Part 143
SDWA requirements for Certification of Metals
January 2002

***Primary** Contaminants with MCL values (141.62):*
Shall be analyzed to determine compliance with the MCLs listed in 141.62. The MCL for arsenic will become 0.010 mg/L on January 23, 2006. Must use methods in table 141.23(k)(1).

2009

Parameter	Calibration Standards(mg/L)	MCL(mg/L)	MDL(mg/L)*		
Antimony (200.8,.9)	Blk;	0.006	~~.002~~ .00122	31138 fur	
Arsenic (200.7,.8,.9)	Blk;	0.01	.00038	31138	.38 ppb 6-3-09
Barium (200.7,.8)	Blk;	2	.0005	200.7	
Beryllium (200.7,.8,.9)	Blk;	0.004	.00003	31138	
Cadmium (200.7,.8,.9)	Blk;	0.005	.000097	31138	
Chromium (200.7,.8,.9)	Blk;	0.1	.00048	31138	
Mercury (245.1,.2.200.8)	Blk;	0.002	.000006	245.1	
Selenium (200.8,.9)	Blk;	0.05	?	31138	
Thallium (200.8,.9)	Blk;	0.002	–	0.47 ppb 8-07-06	

(*MDL - fill in laboratory values for comparison)

***Primary** Contaminants with PQL levels (141.89):*
*SubPart I of 141 - Lead and Copper Rule - If either Pb or Cu exceeds the Action Level, then water system must implement treatment procedure which includes analyzing **calcium** for hardness and **silica** when a silicate compound has been added to the water. Must use methods in table 141.23(k)(1).*

Parameter	Calibration Standards(mg/L)	AL / PQL(mg/L)*	MDL(mg/L)*				
Copper (200.7,.8,.9)	Blk;	1.3 / 0.050	200.7 .000004 FUR .00019	3111B 3113B	8.25-09	3111B	.004 mg/L
Lead (200.8,.9)	Blk;	0.015 / 0.005	.00017	3113B	4-29-09		.17 ppb

*AL = Action Level
*PQL = Practical Quantitation Limit
*Must report values as measured between PQL and MDL or ½ PQL.

***Primary** Contaminants for special monitoring - no MCL (141.41):*
Water system must be analyzed for Na at least once a year and reported to EPA. Must use methods in table 141.23(k)(1).

Parameter	Calibration Standards(mg/L)	MDL(mg/L)	
Sodium	Blk;	.07	3111B

*Optional **Primary** Contaminants which must be certified if they are to be reported - no MCL (141.23(k)(3)):*
These are to be listed as a primary if they are to be certified.

Parameter	Calibration Standards(mg/L)	MDL(mg/L)
Calcium	Blk;	
Nickel	Blk;	
Magnesium	Blk;	
Silica	Blk;	

***Secondary** Contaminants - primarily affect aesthetic quality unless very high concentrations. Can use any method and they don't need to be certified (Part 143). Report as Acceptable or Not.*
"The regulations are not Federally enforceable but are intended as guidelines for the states." (SMCL table - 143.3.)

Parameter	Calibration Standards(mg/L)	SMCL (mg/L)	MDL(mg/L)
Aluminum	Blk;	0.05-0.2	
Copper *(also a primary)*	Blk;	1.0	
Iron	Blk;	0.3	
Manganese	Blk;	0.05	
Silver	Blk;	0.1	
Zinc	Blk;	5.0	

WV00003 Health Lab Big Chimney Inorganic Contaminants

Analyte Name	PT Evaluation	PT Cert Status	PT Method Description	On-Site Cert Status 9/19/06	On-Site Method Description	Overall Certification 1/1/09 to12/31/09	Certification Method
Antimony	Acceptable	C	SM 3113 B	C	SM 3113 B	C	3113B
Arsenic	Acceptable	C	SM 3113 B	C	SM 3113 B	C	3113B
Asbestos	Not Reported	NC		NC	Not Reviewed	NC	
Barium	Acceptable	C	EPA 200.7	C	EPA 200.7	C	EPA 200.7
Beryllium	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Cadmium	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Chromium	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Copper	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Copper	Acceptable	C	SM 3111 B	C	SM 3111 B	C	SM 3111 B
Cyanide (Free) ISE	Acceptable	C	SM 4500 CN F	C	SM 4500 CN F	C	SM 4500 CN F
Cyanide (Total, Require if screen) ISE not distilled	Not Reported	NC		NC	Not Reviewed	C	**Total CN only required if used for screening.**
Fluoride	Acceptable	C	EPA 300.0	C	EPA 300.0	C	EPA 300.0
Lead	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Mercury	Acceptable	C	EPA 245.1	C	EPA 245.1	C	EPA 245.1
Nickel	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Nitrate	Acceptable	C	EPA 300.0	IC	EPA 300.0	IC	EPA 300.0
Nitrate	Acceptable	C	EPA 353.2	C	EPA 353.2	C	EPA 353.2
Nitrite	Acceptable	C	EPA 300.0	IC	EPA 300.0	IC	EPA 300.0
Nitrite	Acceptable	C	EPA 353.2	IC	EPA 353.2	IC	EPA 353.2
Nitrate and Nitrite (Total) Diff. PT	Acceptable	C	EPA 353.2	C	EPA 353.2	C	EPA 353.2
Selenium	Acceptable	C	SM 3113 B	C	SM 3113 B	C	SM 3113 B
Sodium	Acceptable	C	SM 3111 B	C	SM 3111 B	C	SM 3111 B
Thallium	Not Reported	NC		NC	EPA 200 9	NC	

INORGANIC CHEMICALS:

CONTAMINANT	2009							
	OVERALL CERTIFICATION		PT SAMPLES				ON-SITE REVIEW 9/19/2006	
		Method	A	NA	ND	Method		Method
Antimony	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Arsenic	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Barium	C	EPA200.7	X			EPA200.7	C	EPA200.7
Beryllium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Cadmium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Chromium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Copper	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Copper	C	SM3111B	X			SM3111B	C	SM3111B
Lead	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Mercury	C	EPA245.1	X			EPA245.1	C	EPA245.1
Nitrate	C	EPA353.2	X			EPA353.2	C	EPA353.2
Nitrate	**IC**	EPA300.0	X			EPA300.0	**IC**	EPA300.0
Nitrite	C	EPA353.2	X			EPA353.2	C	EPA353.2
Nitrite	**IC**	EPA300.0	X			EPA300.0	**IC**	EPA300.0
Selenium	C	SM 3113 B	X			SM 3113 B	C	SM 3113 B
Thallium	NC	EPA200.9			X	EPA200.9	NC	EPA200.9
Chloride	AP	EPA300.0	X			EPA300.0	AP	EPA300.0
Sulfate	AP	EPA300.0	X			EPA300.0	AP	EPA300.0
TDS	AP	SM2540C	X			SM2540C	AP	SM2540C
Manganese	AP	SM 3111B	X			SM 3111B	AP	SM 3111B
Nickel	AP	SM 3113B	X			SM 3113B	AP	SM 3113B
Zinc	AP	SM 3111B	X			SM 3111B	AP	SM 3111B
Aluminum	AP	SM 3113B	X			SM 3113B	AP	SM 3113B
Aluminum	**IP**	EPA 200.7	X			EPA 200.7	**IP**	EPA 200.7
Iron	AP	SM 3111B	X			SM 3111B	AP	SM 3111B
Silver	AP	SM 3113B	X			SM 3113B	AP	SM 3113B

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LEAD AND COPPER RULE:

CONTAMINANT	2009							
	OVERALL CERTIFICATION		PT SAMPLES				ON-SITE REVIEW 9/19/2006	
		Method	A	NA	ND	Method		Method
Lead	C	SM3113B	X			SM3113B	C	SM3113B
Copper	C	SM3113B	X			SM3113B	C	SM3113B
Copper	C	SM3111B	X			SM3111B	C	SM3111B
pH	C	EPA150.1	X			EPA150.1	C	EPA150.1
Conductivity	C	SM2510B	X			SM2510B	C	SM2510B
Calcium or Calcium Hardness as $CaCo_3$	C	SM3500 CAD	X			SM3500 CAD	C	SM3500 CAD
Alkalinity	C	SM2320B	X			SM2320B	C	SM2320B
Orthophosphate	**IC**	EPA300.0	X			EPA300.0	**IC**	EPA300.0
Silica	NC							
Temperature (On-Site Only)	NC							
Sodium	C	SM3111B	X			SM3111B	C	SM3111B
Turbidity	C	EPA180.1	X			EPA180.1	C	EPA180.1

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Recovery of an Unknown
PE sample

Method SM3113B **Analyte** Ni

Manufacturer ERA (WS-115)

True Value 42.9 µg/L

Acceptance Limit 36.5 - 49.3 µg/L

Value Reported 43.4 µg/L

Date of Analysis 3/1/06

Alm / 12/4/09

Analyst/ Date

Reviewed by & Title/ Date

Ex. 5 - Deliberative

Nickel
WS-115 (060050) } 43.4 µg/l
+
non-compliance

3-2-06

BLANK QC	0.00		-0.105	-0.105 01Mar06 14:05 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.002	-0.002 01Mar06 14:07 CONCENTRATION LESS THAN IDL				
STANDARD 3 QC	10.00	2.1	0.166	0.161 0.166 01Mar06 14:17	0.167	0.167	0.171	
BLANK QC	0.00		0.002	0.002 01Mar06 14:19 CONCENTRATION LESS THAN IDL				

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Pat Marchio PLW
DATE June 29, 2005
BATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 16 Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	6.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	7.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS
VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7

STANDARD 2	5	20	7
STANDARD 3	10	15	7
STANDARD 4	20	5	7
SAMPLE	20	5	7

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.62 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Ni :

Maximum Ash Temperature : 900 xC
Recommended Atomize Temperature : 2400 xC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 357.7
MOD= 200 Mg/L Pd+Mg +H2
RLV= REPORTING LIMIT VERIFICATION
IDL= 0.27 PPB 05-02-05
MDL= 0.62 PPB 04-04-03 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
RL= REPORTING LIMIT= 2.00 PPB

QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.0 PPB

SAMPLE	CONC ppb	%RSD	MEAN ABS	READINGS			
BLANK QC	0.00		-0.108	-0.108 29Jun05 13:15 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		0.001	0.001 29Jun05 13:17 CONCENTRATION LESS THAN IDL			
STANDARD 1 QC	2.00	6.8	0.022	0.023 29Jun05	0.020 13:24	0.022	
STANDARD 2 QC	5.00	7.0	0.054	0.058 29Jun05	0.051 13:30	0.052	r = 0.9999
STANDARD 3 QC	10.00	3.5	0.105	0.109 29Jun05	0.102 13:36	0.105	
STANDARD 4 QC	20.00	0.2	0.209	0.210 29Jun05	0.209 13:42	0.209	
QCSTANDARD QC	9.29	2.4	0.098	0.096 29Jun05	0.097 13:52	0.101	% R = 92.9
QC BLANK QC	0.29	0.0	0.003	0.003 29Jun05	> IDL, reported 13:54 CONCENTRATION LESS THAN IDL		
BLANK QC	0.00		0.001	0.001 29Jun05	< IDL 14:00 CONCENTRATION LESS THAN IDL		
QC BLANK QC	-0.23	0.0	-0.002	-0.002 29Jun05	> - IDL 14:04 CONCENTRATION LESS THAN IDL		
RICCA 10 PPB QC	10.02	0.0	0.105	0.105 29Jun05	% R = 100.2 14:07		
LAB RF BLANK QC	0.05	0.0	0.001	0.001 29Jun05	< MDL 14:10 CONCENTRATION LESS THAN IDL		
RLV- 2.0 PPB QC	2.06	0.0	0.022	0.022 29Jun05	% R = 103.0 14:12		
LFB 10.0 PPB QC	10.65	0.0	0.112	0.112 29Jun05	% R = 106.5 14:16		
QCSTANDARD QC	9.52	0.0	0.100	0.100 29Jun05	% R = 95.2 14:18		
QC BLANK QC	0.05	0.0	0.001	0.001 29Jun05	< IDL 14:21 CONCENTRATION LESS THAN IDL		
FRW-1 #1 QC	0.13	0.0	0.001	0.001 29Jun05	14:23		

FRW-1 #2 QC	0.3.	0.0	0.003	0.003 29Jun05 14:33 CONCENTRATION LESS THAN IDL	
FRW-1 #3 QC	0.45	0.0	0.005	0.005 29Jun05 14:36 CONCENTRATION LESS THAN IDL	
FRW-1 #4 QC	0.24	0.0	0.003	0.003 29Jun05 14:39 CONCENTRATION LESS THAN IDL	
FRW-1 #5 QC	0.26	0.0	0.003	0.003 29Jun05 14:44 CONCENTRATION LESS THAN IDL	
FRW-1 #6 QC	0.60	0.0	0.007	0.007 29Jun05 14:50 CONCENTRATION LESS THAN IDL	
FRW-1 #7 QC	0.36	0.0	0.004	0.004 29Jun05 14:53 CONCENTRATION LESS THAN IDL	
QCSTANDARD ~~QC~~	10.22	0.0	0.108	0.108 %R = 102.2 29Jun05 14:55	
QC BLANK ~~QC~~	0.33	0.0	0.004	0.004 > IDL, repeated 29Jun05 14:58 CONCENTRATION LESS THAN IDL	
BLANK QC	0.00		0.001	0.001 29Jun05 15:00 CONCENTRATION LESS THAN IDL	
QC BLANK QC	-0.11	0.0	-0.001	-0.001 > -IDL 29Jun05 15:02 CONCENTRATION LESS THAN IDL	
LDR 25 PPB QC	OVER	0.0	0.257	0.257 29Jun05 15:05	LDR - Did not work Repeat another day
LDR 26 PPB QC	OVER	0.0	0.264	0.264 29Jun05 15:08	
LDR 27 PPB QC	OVER	0.0	0.270	0.270 29Jun05 15:10	
LDR 28 PPB QC	OVER	0.0	0.290	0.290 29Jun05 15:12	
LDR 29 PPB QC	OVER	0.0	0.296	0.296 29Jun05 15:14	
LDR 30 PPB QC	OVER	0.0	0.299	0.299 29Jun05 15:17	
LDR 31 PPB QC	OVER	0.0	0.272	0.272 29Jun05 15:19	
LDR 32 PPB QC	OVER	0.0	0.366	0.366 29Jun05 15:22	

FRW-1
$\bar{x}$ = 0.338
S = 0.153
RSD = 45.4
MDL = 0.48
T.V. = 0.5 ppb

Nickel
Non-compliance
MDL DAY 2
0.71

COPY

7-12-05

BLANK QC	0.00		-0.046	-0.046 12Jul05 09:43 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.043	-0.043 12Jul05 09:45 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.002	-0.002 12Jul05 09:47 CONCENTRATION LESS THAN IDL				
STANDARD 3 QC	10.00	2.8	0.172	0.169 0.169 12Jul05 09:57	0.178	0.168	0.176	
BLANK QC	0.00		-0.002	-0.002 12Jul05 10:02 CONCENTRATION LESS THAN IDL				

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Pat Marchio PM
DATE July 12, 2005
BATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 16 Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	6.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	7.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS
VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7

STANDARD 2	5	20	7
STANDARD 3	10	15	7
STANDARD 4	20	5	7
SAMPLE	20	5	7

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.62 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Ni :

Maximum Ash Temperature : 900 xC
Recommended Atomize Temperature : 2400 xC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 357.7
MOD= 200 Mg/L Pd+Mg +H2
RLV= REPORTING LIMIT VERIFICATION
IDL= 0.27 PPB 05-02-05
MDL= 0.62 PPB 04-04-03 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
RL= REPORTING LIMIT= 2.00 PPB

QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.0 PPB

SAMPLE	CONC ppb	%RSD	MEAN ABS	READINGS			
BLANK QC	0.00		-0.095	-0.095 12Jul05 10:06 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		0.003	0.003 12Jul05 10:14 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.004	-0.004 12Jul05 10:16 CONCENTRATION LESS THAN IDL			
STANDARD 1 QC	2.00	7.4	0.039	0.038 12Jul05	0.036 10:23	0.042	
STANDARD 2 QC	5.00	1.1	0.096	0.096 12Jul05	0.096 10:29	0.098	r = 0.998
STANDARD 3 QC	10.00	4.0	0.176	0.183 12Jul05	0.177 10:35	0.169	
STANDARD 4 QC	20.00	1.0	0.314	0.311 12Jul05	0.317 10:43	0.313	
QCSTANDARD QC	9.89	2.8	0.175	0.176 12Jul05	0.179 10:50	0.169	% R = 98.9
QC BLANK QC	0.16	0.0	0.003	0.003 < IDL 12Jul05 10:53 CONCENTRATION LESS THAN IDL			
RICCA 10 PPB QC	8.69	0.0	0.158	0.158 % R = 86.9 , repeated 12Jul05 10:56			
RICCA 10 PPB QC	9.80	0.0	0.174	0.174 % R = 98.0 12Jul05 11:05			
LAB RE BLANK QC	0.09	0.0	0.002	0.002 < MDL 12Jul05 11:08 CONCENTRATION LESS THAN IDL			
RLV- 2.0 PPB QC	1.90	0.0	0.037	0.037 % R = 95.0 12Jul05 11:15			
LFB 10.0 PPB QC	9.66	0.0	0.172	0.172 % R = 96.6 12Jul05 11:17			
QCSTANDARD QC	9.25	0.0	0.166	0.166 % R = 92.5 12Jul05 11:23			
QC BLANK QC	0.02	0.0	0.000	0.000 < IDL 12Jul05 11:26 CONCENTRATION LESS THAN IDL			
050226 QC	0.01	0.0	0.000	0.000 $\bar{x}$ = 0.06 12Jul05 11:32			

QCSPIKE A QC	6.24	0.0	0.119	0.119 %R = 104.0 12Jul05 11:39
050226 LDP QC	-0.01	0.0	-0.000	-0.000 rpd = NV (<RL) 12Jul05 11:42 CONCENTRATION LESS THAN IDL
QCSPIKE A QC	9.62	0.0	0.171	0.171 ~~%R = 96.2, rpd~~ %R = ~~96~~ = 160.3% 12Jul05 11:46 wrong injection volume
QCSPIKE A QC	6.29	0.0	0.119	0.119 %R = 104.8, rpd = 0.80 % 12Jul05 11:54
050226 DDP QC	0.26	0.0	0.005	0.005 rpd = NV(<RL) 12Jul05 11:58 CONCENTRATION LESS THAN IDL
QCSPIKE A QC	6.28	0.0	0.119	0.119 %R = 104.7, rpd = 0.64 % 12Jul05 12:05
050226 LFSM QC	11.28	0.0	0.195	0.195 %R = 112.8 12Jul05 12:10
QCSTANDARD ~~QC~~	10.61	0.0	0.185	0.185 %R = 106.1 12Jul05 12:16
QC BLANK ~~QC~~	0.02	0.0	0.000	0.000 < IDL 12Jul05 12:19 CONCENTRATION LESS THAN IDL
LAB RE BLANK ~~QC~~	0.03	0.0	0.001	0.001 < MDL 12Jul05 12:24 CONCENTRATION LESS THAN IDL
LFB 10.0 PPB ~~QC~~	10.49	0.0	0.183	0.183 %R = 104.9 12Jul05 12:27
FRW-1 #1 QC	0.30	0.0	0.006	0.006 12Jul05 12:30 CONCENTRATION LESS THAN IDL
FRW-1 #2 QC	0.73	0.0	0.014	0.014 12Jul05 13:02
FRW-1 #3 QC	0.83	0.0	0.016	0.016 12Jul05 13:13
FRW-1 #4 QC	0.31	0.0	0.006	0.006 12Jul05 13:17 CONCENTRATION LESS THAN IDL
FRW-1 #5 QC	0.37	0.0	0.007	0.007 12Jul05 13:25 CONCENTRATION LESS THAN IDL
FRW-1 #6 QC	0.40	0.0	0.008	0.008 12Jul05 13:28 CONCENTRATION LESS THAN IDL
FRW-1 #7 QC	0.33	0.0	0.006	0.006 12Jul05 13:35 CONCENTRATION LESS THAN IDL
[illegible]	10.21	0.0	0.179	0.179 %R = 102.1

FRW-1
T.U. = 0.50
$\bar{x}$ = 0.457
S = 0.225
RSD = 49.2
MDL = 0.71

QC BLANK	0.06	0.0	0.001	0.001 < IDL
QC				12Jul05 13:42
				CONCENTRATION LESS THAN IDL

Nickel
non-compliance
MDL - Day 3
3 Day mean = 0.68 ppb

8-9-05

COPY

BLANK QC	0.00		-0.040	-0.040 09Aug05 08:43 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.057	-0.057 09Aug05 08:44 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.002	-0.002 09Aug05 08:46 CONCENTRATION LESS THAN IDL				
STANDARD 3 QC	10.00	3.2	0.136	0.138 0.133 09Aug05 09:07	0.143	0.134	0.133	
BLANK QC	0.00		-0.007	-0.007 09Aug05 09:09 CONCENTRATION LESS THAN IDL				

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Pat Marchio PLM
DATE Aug 9, 2005
BATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 16 Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	6.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	7.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS
VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7

STANDARD 2	5	20	7
STANDARD 3	10	15	7
STANDARD 4	20	5	7
SAMPLE	20	5	7

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.62 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Ni :

Maximum Ash Temperature : 900 xC
Recommended Atomize Temperature : 2400 xC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 354.6
MOD= 200 Mg/L Pd+Mg +H2
RLV= REPORTING LIMIT VERIFICATION
IDL= 0.27 PPB 05-02-05
MDL= 0.62 PPB 04-04-03 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
RL= REPORTING LIMIT= 2.00 PPB

QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.0 PPB

SAMPLE	CONC ppb	%RSD	MEAN ABS	READINGS			
BLANK QC	0.00		0.012	0.012 09Aug05 09:14 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.001	-0.001 09Aug05 09:16 CONCENTRATION LESS THAN IDL			
STANDARD 1 QC	2.00	12.9	0.034	0.037 09Aug05 09:23	0.029	0.035	
STANDARD 2 QC	5.00	4.0	0.080	0.083 09Aug05 09:29	0.080	0.077	r = 0.9994
STANDARD 3 QC	10.00	1.1	0.150	0.148 09Aug05 09:35	0.150	0.151	
STANDARD 4 QC	20.00	0.6	0.278	0.278 09Aug05 09:41	0.279	0.276	
QCSTANDARD QC	10.05	3.0	0.150	0.145 09Aug05 09:48	0.153	0.153	%R = 100.5
QC BLANK QC	-0.07	0.0	-0.001	-0.001 > - IDL 09Aug05 09:51 CONCENTRATION LESS THAN IDL			
RICCA 10 PBB QC	10.66	0.0	0.159	0.159 %R = 106.6 09Aug05 10:03			
LAB RE BLANK QC	0.34	0.0	0.006	0.006 < MDL 09Aug05 10:05 CONCENTRATION LESS THAN IDL			
RLV- 2.0 PPB QC	1.91	0.0	0.032	0.032 %R = 95.5 09Aug05 10:07			
LFB 10.0 PPB QC	11.21	0.0	0.166	0.166 %R = 112.1 09Aug05 10:09			
QCSTANDARD QC	10.30	0.0	0.154	0.154 %R = 103.0 09Aug05 10:12			
QC BLANK QC	-0.10	0.0	-0.002	-0.002 > - IDL 09Aug05 10:15 CONCENTRATION LESS THAN IDL			
050282 0 QC	2.03 $\bar{X}_i$ = 2.58	0.0	0.034	0.034 09Aug05 10:17			standard additions $\bar{X}_i$ = 2.76 = 0.003 ppm
QCSPIKE A 6 QC	9.08	0.0	0.137	0.137 %R = 117.5 09Aug05 10:19			r = 0.996
QCSPIKE B 12 QC	14.90	0.0	0.213	0.213 %R = 107.2 09Aug05 10:23			

... 2.92

... = 12 3/6 %, repeat

QC					09Aug05 10:30
050282 DDP QC	2.35 $X_1' = 2.92$	0.0	0.039	0.039 09Aug05 10:39	, rpd = 12.36
050282 LFSM QC	12.29 $X_1' = 12.36$	0.0	0.180	0.180 09Aug05 10:45	%R = 96.1
050282 LDP QC	2.19 $X_1' = 2.78$	0.0	0.037	0.037 09Aug05 11:02	rsd of All duplicates = 6.19 %
LAB RE BLANK QC	0.09	0.0	0.002	0.002 09Aug05 11:10 CONCENTRATION LESS THAN IDL	< MDL
LFB 10.0 PPB QC	11.32	0.0	0.167	0.167 09Aug05 11:12	%R = 113.2
QCSTANDARD QC	10.78	0.0	0.160	0.160 09Aug05 11:15	%R = 107.8
QC BLANK QC	-0.00	0.0	-0.000	-0.000 09Aug05 11:17 CONCENTRATION LESS THAN IDL	< IDL
050290 QC	0 0.20 $X_1' = 0.33$	0.0	0.003	0.003 09Aug05 11:20 CONCENTRATION LESS THAN IDL	$\bar{X} = 0.19 < 0.002$ ppm RL
QCSPIKE A QC	6 7.55	0.0	0.116	0.116 09Aug05 11:22	%R = 125.8
QCSPIKE B QC	12 14.81	0.0	0.212	0.212 09Aug05 11:26	%R = 123.4
					r = 0.999
050290 LDP QC	-0.11 $X_1' = 0.03$	0.0	-0.002	-0.002 09Aug05 11:29 CONCENTRATION LESS THAN IDL	, rpd = NV (< RL)
QCSPIKE A QC	7.41	0.0	0.114	0.114 09Aug05 11:33	rpd = 1.87 %
050290 DDP QC	0.34 $X_1' = 0.51$	0.0	0.006	0.006 09Aug05 11:36 CONCENTRATION LESS THAN IDL	rpd = NV (< RL)
QCSPIKE A QC	7.55	0.0	0.116	0.116 09Aug05 11:41	rpd = 0.00 %
050290 LFSM QC	12.15 $X_1' = 10.38$	0.0	0.178	0.178 09Aug05 11:44	%R = 103.8
QCSTANDARD QC	10.99	0.0	0.163	0.163 09Aug05 11:47	%R = 109.9
QC BLANK QC	0.28	0.0	0.005	0.005 09Aug05 11:50 CONCENTRATION LESS THAN IDL	> IDL
QC BLANK QC	0.21	0.0	0.004	0.004 09Aug05 11:54 CONCENTRATION LESS THAN IDL	< IDL
LAB RE BLANK QC	0.09	0.0	0.002	0.002 09Aug05 11:57	< MDL

LFB 10.0 PPB QC	11.39	0.0	0.168	0.168 %R = 113.9 09Aug05 11:59
FRW-1 #1 QC	0.58	0.0	0.010	0.010 09Aug05 12:01 CONCENTRATION LESS THAN IDL
FRW-1 #2 QC	0.42	0.0	0.007	0.007 09Aug05 12:16 CONCENTRATION LESS THAN IDL
FRW-1 #3 QC	0.70	0.0	0.012	0.012 09Aug05 12:29
FRW-1 #4 QC	0.39	0.0	0.007	0.007 09Aug05 12:44 CONCENTRATION LESS THAN IDL
FRW-1 #5 QC	0.35	0.0	0.006	0.006 09Aug05 12:50 CONCENTRATION LESS THAN IDL
FRW-1 #6 QC	1.09	0.0	0.018	0.018 09Aug05 12:58
FRW-1 #7 QC	0.35	0.0	0.006	0.006 09Aug05 13:01 CONCENTRATION LESS THAN IDL
QCSTANDARD QC	10.40	0.0	0.155	0.155 %R = 104.0 09Aug05 13:07
QC BLANK QC	-0.03	0.0	-0.001	-0.001 > IDL 09Aug05 13:09 CONCENTRATION LESS THAN IDL

MDL
$\bar{x} = 0.554$
$S = 0.27$
RSD = 48.1%
$S \times 3.14 = 0.85$

MDL	3 Day Mean
6/29/05	0.48 ppb
7/12/05	0.71 ppb
8/9/05	0.85 ppb

$0.68 = \bar{X}$

Method Detection Limit
Data Summary

Method SM3113B Analyte Ni

Analyst Pim Intsrument Varian 400+

True Value of Fortified Reagent Water (FRW)
used 0.50 µg/L

Date.....	Mean of 7 replicates	Standard Deviation	%RSD	MDL
6/29/05	0.388	0.153	45.4	0.48
7/12/05	0.457	0.225	49.2	0.71
8/9/05	0.554	0.27	48.1	0.85

MDL = Standard Deviation X Student t Value (3.14)

MDL average from 3 non-consecutive days = 0.68 µg/L

Nickel
MDL - Day 1
MDL = 0.48 ppb
6-30-05

BLANK QC	0.00		-0.106	-0.106 29Jun05 12:56 CONCENTRATION LESS THAN IDL
BLANK QC	0.00		-0.003	-0.003 29Jun05 12:58 CONCENTRATION LESS THAN IDL
STANDARD 3 QC	10.00	4.5	0.114	0.112 0.111 0.108 0.119 0.120 29Jun05 13:08
BLANK QC	0.00		0.004	0.004 29Jun05 13:11 CONCENTRATION LESS THAN IDL

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Pat Marchio PLM
DATE March 01,2006
BATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 16 Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	5.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	7.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS

VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7
STANDARD 1	20	5	7
STANDARD 2	5	20	7
STANDARD 3	10	15	7
STANDARD 4	20	5	7
SAMPLE	20	5	7

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.62 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Ni :

Maximum Ash Temperature : 900 xC
Recommended Atomize Temperature : 2400 xC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 357.7
MOD= 200 Mg/L Pd+Mg +H2
RLV= REPORTING LIMIT VERIFICATION
IDL= 0.27 PPB 05-02-05
MDL= 0.68 PPB 08-09-05 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
RL= REPORTING LIMIT= 2.00 PPB

QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.0 PPB

SAMPLE	CONC ppb	%RSD	MEAN ABS	READINGS			
BLANK QC	0.00		-0.108	-0.108 01Mar06 14:26 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.004	-0.004 01Mar06 14:31 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.000	-0.000 01Mar06 14:33 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		0.002	0.004 01Mar06 14:39 CONCENTRATION LESS THAN IDL	-0.001	0.001	
STANDARD 1 QC	2.00	6.4	0.029	0.030 01Mar06 14:45	0.027	0.029	r = 0.9995
STANDARD 2 QC	5.00	1.8	0.072	0.072 01Mar06 14:52	0.071	0.074	
STANDARD 3 QC	10.00	1.6	0.148	0.150 01Mar06 14:57	0.149	0.145	
STANDARD 4 QC	20.00	1.8	0.281	0.286 01Mar06 15:04	0.276	0.280	
QCSTANDARD ~~QC~~	9.92	4.9	0.147	0.139 01Mar06 15:11	0.152	0.149	%R = 99.2
QC BLANK ~~QC~~	-0.02	0.0	-0.000	-0.000 01Mar06 15:14 CONCENTRATION LESS THAN IDL			> - IDL
RICCA10.0PPB ~~QC~~	9.81	0.0	0.145	0.145 01Mar06 15:16			%R = 98.1
LAB RE BLANK QC	-0.10	0.0	-0.001	-0.001 01Mar06 15:18 CONCENTRATION LESS THAN IDL			< MDL
RLV- 2.0 PPB ~~QC~~	1.98	0.0	0.028	0.028 01Mar06 15:20			%R = 99.0
LFB 10.0 PPB ~~QC~~	8.64	0.0	0.127	0.127 01Mar06 15:22			%R = 86.4
QCSTANDARD	9.67	0.0	0.143	0.143			%R = 96.7

QC BLANK QC	0.01	0.0	0.000	0.000 < IDL 01Mar06 15:28 CONCENTRATION LESS THAN IDL
060050 20X QC	2.18	0.0	0.031	0.031 01Mar06 15:32
060050 4X QC	11.12	0.0	0.164	0.164 $\bar{x}$ = 10.85×4 = 43.4 µg/l 01Mar06 15:40
QCSPIKE A QC	16.67	0.0	0.238	0.238 %R = 92.5 01Mar06 15:42
060050 LDP QC	10.56	0.0	0.156	0.156 rpd = 4.98% 01Mar06 15:45
060050 DDP QC	10.89	0.0	0.161	0.161 rpd = 2.09% 01Mar06 15:48
060050 LFSM QC	13.44 ×4 = 53.76	0.0	0.195	0.195 %R = 103.6 01Mar06 15:53
LAB RE BLANK QC	0.05	0.0	0.001	0.001 < MDL 01Mar06 15:56 CONCENTRATION LESS THAN IDL
LFB 10.0 PPB QC	9.96	0.0	0.147	0.147 %R = 99.6 01Mar06 15:58
QCSTANDARD QC	9.94	0.0	0.147	0.147 %R = 99.4 01Mar06 16:00
QC BLANK QC	-0.03	0.0	-0.000	-0.000 > -IDL 01Mar06 16:03 CONCENTRATION LESS THAN IDL
060003 QC	-0.14	0.0	-0.002	-0.002 $\bar{x}$ = -0.05, < 0.002 mg/l 01Mar06 16:05 CONCENTRATION LESS THAN IDL
QCSPIKE A QC	6.79	0.0	0.099	0.099 %R = 113.2 01Mar06 16:07
060003 LDP QC	0.04	0.0	0.001	0.001 rpd = NV(<RL) 01Mar06 16:10 CONCENTRATION LESS THAN IDL
QCSPIKE A QC	6.69	0.0	0.097	0.097 rpd = 1.48% 01Mar06 16:12
060003 DDP QC	-0.10	0.0	-0.001	-0.001 rpd = NV(<RL) 01Mar06 16:14 CONCENTRATION LESS THAN IDL
QCSPIKE A QC	7.06	0.0	0.103	0.103 rpd = 3.90% 01Mar06 16:16
060003 LFSM QC	10.50	0.0	0.155	0.155 %R = 105.0 01Mar06 16:18
QCSTANDARD QC	10.08	0.0	0.149	0.149 %R = 100.8 01Mar06 16:21
QC BLANK	0.36	0.0	0.005	0.005 > IDL, repeated

Nickel
WS-151 = 220.0 µg/L
(W900237-01-001)
P.T. 2009

BLANK QC	0.00		0.007	-0.0[illegible] 12Mar09 [illegible] CONCENTRATION LESS THAN IDL
BLANK QC	0.00		0.007	-0.007 12Mar09 [illegible] CONCENTRATION LESS THAN IDL
BLANK QC	0.00		0.007	0.007 12Mar09 [illegible] CONCENTRATION LESS THAN IDL
BLANK QC	0.00		-0.004	-0.004 12Mar09 [illegible] CONCENTRATION LESS THAN IDL
STANDARD QC	[illegible]	1.3	0.18[illegible]	0.18[illegible] [illegible] 0.18[illegible] [illegible] 0.18[illegible] 12Mar09 [illegible]
BLANK QC	0.00		0.00[illegible]	0.00[illegible] 12Mar09 [illegible] CONCENTRATION LESS THAN IDL

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Raf Marchio RM
DATE Mar 12,2009
CATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM to Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	6
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	6.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	2.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS
VOLUMES (µL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7
STANDARD	20	5	7

STANDARD 3	10	1[illegible]	7
STANDARD 4	20	5	7
SAMPLE	2[illegible]	5	7

RECALIBRATION RATE 0
RECHECK RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	53
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	53
QC STANDARD VOLUME (µL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (µL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.63 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Pb :

Maximum Ash Temperature : 900 oC
Recommended Atomize Temperature : 2400 oC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 404.6 MOD= 200mg/L Pd+Mg+HNO
QC SPIKE A= 6PPB, prepare by 6uL injection of 20 PPB STD
QC SPIKE B= 12PPB, prepare by 12uL injection of 20 PPB STD
IDL= 0.34 PPB 04-05-06
MDL= 0.63 PPB 08-09-05 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
QCS LOT # J.T. Baker LFB/LFM= 10PPB

E026617

[illegible]	LONG PPB	[illegible]	MEAN MGS	READINGS		
[illegible]	[illegible]		0.077	[illegible] 12Mar09 [illegible] CONCENTRATION LESS THAN [illegible]		
BLANK QC	[illegible]		[illegible]	[illegible] 12Mar09 [illegible] CONCENTRATION LESS THAN [illegible]		
BLANK QC	0.00		0.001	0.001 12Mar09 13:15 CONCENTRATION LESS THAN IDL		
STANDARD QC	[illegible]	7.2	0.031	[illegible] 12Mar09 13:32	[illegible]	[illegible]
STANDARD 2 QC	[illegible]		0.077	[illegible] 12Mar09 [illegible]	0.077	[illegible]
STANDARD 3 QC	[illegible]	.6	[illegible]	[illegible] 12Mar09 [illegible]	[illegible]	[illegible]
STANDARD 4 QC	[illegible]	1.4	[illegible]	[illegible] 12Mar09 [illegible]	[illegible]	[illegible]
IPC 10.00PPB QC	[illegible]	4.3	[illegible]	[illegible] 12Mar09 13:49	[illegible]	0.166 %R = 95.5
QC BLANK QC	-0.24	0.0	-0.004	-0.004 12Mar09 13:51 CONCENTRATION LESS THAN IDL		>- IDL
QCS 10.0PPB QC	11.39	0.0	0.192	0.192 12Mar09 13:59		%R = 113.9, repeated
QCS 10.0PPB QC	10.44	0.0	0.176	0.176 12Mar09 14:11		%R = 104.4
LEI QC	0.20	0.0	0.003	0.002 12Mar09 14:13 CONCENTRATION LESS THAN IDL		<MDL
MWL - [illegible].00PPB QC	[illegible]	0.0	0.036	0.036 12Mar09 14:16		%R = 116.0
LEBMR 2.0PPB QC	2.42	0.0	[illegible]	[illegible] 12Mar09 14:22		%R = 121.0
LEI 10.0 PPB QC	11.01	0.0	0.186	0.186 12Mar09 14:25		%R = 110.1
IPC 10.00PPB QC	10.26	0.0	0.173	0.173 12Mar09 14:28		%R = 102.6
QC BLANK QC	-0.13	0.0	-0.002	-0.002 12Mar09 14:31 CONCENTRATION LESS THAN IDL		>- IDL
237-01	OVER	0.0	1.062	1.062		

$r^2 = 0.9998$

[illegible]	[illegible]	0.0	0.184	0.184 12Mar09 14:[illegible]	$\bar{x}$ = 10.98×20 = ~~219~~ 219.6 = 220 µg/L
QC SPIKE A QC	16.46	0.0	0.280	0.280 12Mar09 14:[illegible]	%R = 92.8
-01 [illegible] QC	[illegible]	0.0	0.187	0.187 12Mar09 14:42	rpd = 1.64%
-01 DPP QC	11.17	0.0	0.189	0.189 12Mar09 14:46	rpd = 2.54%
-01 LFM QC	12.01	0.0	0.203	0.203 12Mar09 14:[illegible]	%R = NV (spike <25% Analyte conc)
[illegible] QC	[illegible]	0.0	0.167	0.167 12Mar09 14:49	%R = 99.4
QC BLANK Q	[illegible]	0.0	0.003	0.003 12Mar09 14:51 CONCENTRATION LESS THAN IDL	< IDL

Copy: Original in 2005 files

Nickel
IDL = 0.27
+
IDC

5-3-05

BLANK QC	0.00		0.391	0.391 02May05 11:12 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.483	-0.483 02May05 11:14 CONCENTRATION LESS THAN IDL				
BLANK QC	0.00		-0.007	-0.007 02May05 11:17 CONCENTRATION LESS THAN IDL				
STANDARD 3 QC	10.00	2.6	0.157	0.153 0.156 02May05 11:28	0.158	0.163	0.153	
BLANK QC	0.00		0.002	0.002 02May05 11:30 CONCENTRATION LESS THAN IDL				

Initial Demonstration of Capability
For Precision and Accuracy
Data Summary

Method SM3113B **Analyte** Ni

Quality Control Sample (lot#) Ricca 3403330

True Value 10.0 µg/L

Date QC Sample Made 3/21/05

Date QC Sample Digested 3/22/05

Date of Analysis 5/2/05

Replicate	Concentration µg/L	Percent Recovery
1	10.43	104.3
2	10.72	107.2
3	10.35	103.5
4	10.46	104.6

Mean Recovery 104.9 **Accuracy Limit** 100 ± 10%

% RSD 1.53% **Precision Limit** < 5% RSD

Pcm 12/4/09
Analyst/ Date

Program Manager/ Date

Varian SpectrAA 300/400
QC Protocol Report

OPERATOR Pat Marchio PLM
DATE May 2 , 2005
BATCH Ni

QC PROTOCOL PARAMETERS

IF THERE IS AN ERROR	STOP
QC SPIKE POSITION	52
RECOVERY LIMITS (%)	85 TO 115
RECOVERY MINIMUM LIMIT (%)	40
CORRELATION COEFFICIENT (r)	0.995
OVERRANGE VOLUME REDUCTION	2
REPLICATE RSD LIMIT (%)	20.0

PROGRAM 16 Ni 2.00-20.00 ppb

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	PEAK HEIGHT
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.2
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	232.0
SAMPLE INTRODUCTION	SAMPLER AUTOMIXING
TIME CONSTANT	0.05
MEASUREMENT TIME (sec)	1.0
REPLICATES	3
BACKGROUND CORRECTION	ON

FURNACE PARAMETERS

STEP NO.	TEMPERATURE (C)	TIME (sec)	GAS FLOW (L/min)	GAS TYPE	READ COMMAND
1	130	25.0	3.0	ALTERNATE	NO
2	130	5.0	3.0	ALTERNATE	NO
3	150	6.0	3.0	ALTERNATE	NO
4	900	6.0	3.0	ALTERNATE	NO
5	900	7.0	3.0	ALTERNATE	NO
6	900	2.0	3.0	NORMAL	NO
7	900	1.0	0.0	NORMAL	NO
8	2550	1.2	0.0	NORMAL	YES
9	2550	3.0	0.0	NORMAL	YES
10	2550	2.0	3.0	NORMAL	NO
11	2400	2.0	3.0	NORMAL	NO

SAMPLER PARAMETERS

VOLUMES (fL)

	SOLUTION	BLANK	MODIFIER
BLANK	--	25	7
STANDARD 1	2	23	7
STANDARD 2	5	20	7
STANDARD 3	10	15	7
STANDARD 4	20	5	7
SAMPLE	20	25	7

RECALIBRATION RATE 0
RESLOPE RATE 0

MULTIPLE INJECT NO HOT INJECT YES PRE INJECT NO
TEMPERATURE 96
INJECT RATE 2

QC PROTOCOL PARAMETERS

QC STANDARD RATE	10
QC INITIAL STANDARD POSITION	52
QC INITIAL BLANK POSITION	51
QC CONTINUING STANDARD POSITION	52
QC CONTINUING BLANK POSITION	51
QC STANDARD VOLUME (fL)	10
QC STANDARD CONCENTRATION	10.00 ppb
QC STANDARD LIMITS (%)	90 TO 110
QC SPIKE RATE	1
QC SPIKE VOLUME (fL)	6
QC SPIKE CONCENTRATION	20.00 ppb
MATRIX SPIKE CONCENTRATION	0.00 ppb
INSTRUMENT DETECTION LIMIT	0.62 ppb
REQUIRED DETECTION LIMIT	0.00 ppb

CONDITIONS FOR Ni :

Maximum Ash Temperature : 900 xC
Recommended Atomize Temperature : 2400 xC

Response with Argon :
10 microlitres of 50 micrograms/litre gives about 0.2 ABS.

PMV= 364.0
MOD= 200 Mg/L Pd+Mg +H2
RLV= REPORTING LIMIT VERIFICATION
IDL= 0.39 PPB 01-17-02
MDL= 0.62 PPB 04-04-03 3DAY MEAN
LDR LIMIT= 30.00 PPB 04-08-02
RL= REPORTING LIMIT= 2.00 PPB

QCSPIKE A= 6.00 PPB
QCSPIKE B= 12.0 PPB

SAMPLE	CONC PPD	%RSD	MEAN ABS	READINGS			
BLANK QC	0.00		-0.099	-0.099 02May05 11:34 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.001	-0.001 02May05 11:37 CONCENTRATION LESS THAN IDL			
BLANK QC	0.00		-0.000	-0.001 02May05 11:44 CONCENTRATION LESS THAN IDL	-0.000	0.000	
STANDARD 1 QC	2.00	7.2	0.049	0.051 02May05 11:51	0.051	0.045	r = 0.9995
STANDARD 2 QC	5.00	3.8	0.081	0.083 02May05 11:58	0.083	0.078	
STANDARD 3 QC	10.00	4.0	0.152	0.147 02May05 12:04	0.150	0.159	
STANDARD 4 QC	20.00	0.3	0.281	0.280 02May05 12:11	0.281	0.282	
QCSTANDARD ~~QC~~	0.06	99.9	0.002	0.005 02May05 12:31 CONCENTRATION LESS THAN IDL	-0.000	-0.000	Did not reposition std. in autosampler, repeat
QCSTANDARD ~~QC~~	10.16	2.9	0.154	0.156 02May05 12:40	0.149	0.157	% R = 101.6
QC BLANK ~~QC~~	0.12	0.0	0.003	0.003 02May05 12:43 CONCENTRATION LESS THAN IDL	< IDL		
RICCA 10 PPB QC	11.49	0.0	0.172	0.172 02May05 12:46	% R = 114.9		
RICCA 10 PPB QC	11.48	0.0	0.171	0.171 02May05 12:49	% R = 114.8		
WS 103 20X ~~QC~~	TV: 332 17.95 359	0.0	0.255	0.255 02May05 12:55	% R 108.1	, was OK	
WS 103 20X ~~QC~~	18.46 369.2	0.0	0.261	0.261 02May05 12:57	% R = 111.2		
BLANK QC	0.00		0.003	0.003 02May05 13:00 CONCENTRATION LESS THAN IDL			

Re-calibrated instrument

STANDARD 1 QC	2.00	12.9	0.031	0.030	0.027	0.035

STANDARD 2 QC	5.00	8.0	0.085	0.083 02May05 13:14	0.080	0.093	
STANDARD 3 QC	10.00	1.0	0.151	0.151 02May05 13:20	0.150	0.153	0.9990
STANDARD 4 QC	20.00	1.7	0.290	0.294 02May05 13:26	0.290	0.284	
QCSTANDARD QC	-0.06	99.9	-0.001	0.001 02May05 13:34 CONCENTRATION LESS THAN IDL	-0.003	-0.001	Did not reposition std. in autosampler, repeat
QCSTANDARD QC	10.13	2.2	0.153	0.157 02May05 13:41	0.152	0.150	%R = 101.3
QC BLANK QC	-0.13	0.0	-0.002	-0.002 02May05 13:43 CONCENTRATION LESS THAN IDL			> -IDL
T.V = 332 WS 103 20X QC	17.73 354.6	0.0	0.259	0.259 02May05 13:46			%R = 106.8
RICCA 10PPM QC	9.82	0.0	0.149	0.149 02May05 13:50			%R = 98.2
LAB RE BLANK QC	-0.06	0.0	-0.001	-0.001 02May05 13:52 CONCENTRATION LESS THAN IDL			< MDL
RLV- 2.0 PPB QC	1.73	0.0	0.027	0.027 02May05 13:54			%R = 86.5
LFB 10.0PPB QC	10.76	0.0	0.162	0.162 02May05 13:57			%R = 107.6
QCSTANDARD QC	9.70	0.0	0.147	0.147 02May05 14:00			%R = 97.0
QC BLANK QC	0.10	0.0	0.002	0.002 02May05 14:02 CONCENTRATION LESS THAN IDL			< IDL
IDC #1 TV = 10.6 QC	10.43	0.0	0.157	0.157 02May05 14:05			%R = 104.3
IDC #2 QC	10.72	0.0	0.161	0.161 02May05 14:07			%R = 107.2
IDC #3 QC	10.35	0.0	0.156	0.156 02May05 14:09			%R = 103.5
IDC #4 QC	10.46	0.0	0.158	0.158 02May05 14:11			%R = 104.6
QCSTANDARD QC	9.93	0.0	0.150	0.150 02May05 14:16			%R = 99.3
QC BLANK QC	-0.11	0.0	-0.002	-0.002 02May05 14:19 CONCENTRATION LESS THAN IDL			> -IDL
IDL BLANK 1 QC	-0.04	0.0	-0.001	-0.001 02May05 14:21			

RSD = 1.53%

IDL BLANK 2 QC	-0.02	0.0	-0.000	-0.000 02May05 14:23 CONCENTRATION LESS THAN IDL	
IDL BLANK 3 QC	-0.02	0.0	-0.000	-0.000 02May05 14:27 CONCENTRATION LESS THAN IDL	
IDL BLANK 4 QC	0.04	0.0	0.001	0.001 02May05 14:33 CONCENTRATION LESS THAN IDL	
IDL BLANK 5 QC	-0.02	0.0	-0.000	-0.000 02May05 14:38 CONCENTRATION LESS THAN IDL	
IDL BLANK 6 QC	0.08	0.0	0.001	0.001 02May05 14:41 CONCENTRATION LESS THAN IDL	$S_{10} = 0.091$
IDL BLANK 7 QC	0.24	0.0	0.004	0.004 02May05 14:45 CONCENTRATION LESS THAN IDL	$S_{10} \cdot 3 = 0.27$
IDL BLANK 8 QC	0.17	0.0	0.003	0.003 02May05 14:52 CONCENTRATION LESS THAN IDL	
IDL BLANK 9 QC	0.09	0.0	0.001	0.001 02May05 14:54 CONCENTRATION LESS THAN IDL	
IDL BLANK 10 QC	0.07	0.0	0.001	0.001 02May05 14:56 CONCENTRATION LESS THAN IDL	
QCSTANDARD ~~QC~~	10.83	0.0	0.163	0.163 %R = 108.3 02May05 14:59	
QC BLANK QC	-0.11	0.0	-0.002	-0.002 > - IDL 02May05 15:01 CONCENTRATION LESS THAN IDL	

West Virginia
Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Laboratory

Standard Operating Procedure

Metals
By
Inductively Coupled Plasma / Mass Spectrometry
Following
EPA Method 200.8 Revision 5.4

APPROVED:

10-14-10
HHR Program Manager - Environmental Chemistry Date

10-20-2010
HHR Program Manager - Quality Control Coordinator Date

10-15-2010
HHR Laboratory Director III Date

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Table of Contents

1. SCOPE AND APPLICATION 5
2. SUMMARY OF METHOD 5
3. INTERFERENCES 6
4. SAFETY 6
4.1. PROTECTIVE EQUIPMENT 6
4.2. CHEMICALS 6
5. SAMPLE HANDLING 7
5.1. SAMPLE COLLECTION 7
5.2. SAMPLE PRESERVATION 7
5.3. PRESERVATION VERIFICATION 7
5.4. SAMPLE STORAGE 7
5.5. SAMPLE REJECTION 7
6. EQUIPMENT AND SUPPLIES 8
6.1. EQUIPMENT 8
6.2. SUPPLIES 8
7. REAGENTS AND STANDARDS 8
7.1. REAGENTS 9
7.2. SOLUTIONS 9
8. INITIAL DEMONSTRATION OF CAPABILITY (IDC) 11
8.1. LINEAR CALIBRATION RANGE 11
8.2. INSTRUMENT DETECTION LIMIT (IDL) 11
8.3. METHOD DETECTION LIMIT (MDL) 12
8.4. INITIAL DEMONSTRATION OF ACCURACY 12
8.5. INITIAL DEMONSTRATION OF PRECISION 13
8.6. ANALYSIS OF AN UNKNOWN 14
9. QUALITY CONTROLS 14
9.1. QUALITY CONTROL BLANK (QC BLANK) 14
9.2. LABORATORY REAGENT BLANK (LRB) 15
9.3. LABORATORY FORTIFIED BLANK (LFB) 15
9.4. MINIMUM REPORT LIMIT (MRL) 16
9.5. LABORATORY FORTIFIED SAMPLE MATRIX (LFM) 16
9.6. QUALITY CONTROL SAMPLE (QCS) 17
9.7. INITIAL CALIBRATION VERIFICATION (ICV) 18
9.8. CONTINUING CALIBRATION VERIFICATION (CCV) 18
9.9. INTERNAL STANDARD (IS) 19
9.10. DUPLICATED (DUP) 19
9.11. CORRECTIVE ACTION LOG BOOK 20
10. PROCEDURE 20
10.1. SAMPLE DIGESTION 20
10.2. INSTRUMENT STARTUP 21
10.3. TUNING AND OPTIMIZING SYSTEM 22
10.4. PERFORMING ROUTING ANALYSES 23
11. DATA ANALYSIS AND CALCULATIONS 24
11.1. DATA ANALYSIS 24

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0484

11.2. CALCULATIONS 25
12. TROUBLESHOOTING AND MAINTENANCE 26
13. REFERENCES 26
APPENDIX A - QUALITY CONTROL LIMITS AND CORRECTIVE ACTION SUMMARY 28
APPENDIX B - TABLE OF THE ISOTOPES MONITORED, CORRECTION EQUATIONS USED, AND POTENTIAL INTERFERENCES 29
APPENDIX C - OPERATING PARAMETERS FOR THE ELAN 9000 ICP-MS INSTRUMENT 31
APPENDIX D - DAILY PERFORMANCE CRITERIA 31
APPENDIX E – SMARTTUNE DAILY WIZARD SETTINGS 32

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0485

1. Scope and Application

1.1. This Standard Operating Procedure (SOP) describes the daily operation, tuning, optimization, and procedures for the analysis of drinking water samples according to U.S. EPA Method 200.8 revision 5.4,1994 for the elements listed in Appendix A using the ELAN® 9000 ICP-MS.

1.2. All aqueous samples must be acidified (preserved) within two weeks of collection. All samples are digested for total recoverable metals. ~~& sit for how long~~ ?

1.3. Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L.

1.4. The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.5. Routine operation and maintenance procedures for the ELAN® 9000 ICP-MS may be found in the ELAN® Hardware Manual provided by the instrument manufacturer.

1.6. Detailed instructions for operating the ELAN® 9000 ICP-MS software may be found in the ELAN® Version 3.4 Software Guide

1.7. This SOP was written using revision 5.4 (1994) of EPA Method 200.8 "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry" and the 5th edition of the EPA's "Manual for the Certification of Laboratories Analyzing Drinking Water: Criteria and Procedures Quality Assurance."

1.8. Each analyst using this SOP will need to generate and have on file the initial performance data described in section 8.1 before the analysis of any samples.

1.9. This SOP applies to the following metals: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn

2. Summary of Method

An aliquot of a well mixed, homogeneous aqueous sample is accurately measured for sample processing. For total recoverable analysis an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, mixed and if needed, centrifuged or allowed to settle overnight prior to analysis.

Aqueous sample digestates are nebulized into a spray chamber where a stream of argon carries the sample aerosol through a quartz torch and injects it into a radio frequency plasma. There the sample is decomposed and desolvated. The ions produced are entrained in the plasma gas and by means of a water cooled,

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Freedom_0006095_0486

differentially pumped interface, introduced into a high-vacuum chamber that houses a quadrupole mass spectrometer. The ions are sorted according to their mass-to-charge ratio and measured with a detector.

3. Interferences

3.1. Isobaric Interferences occur when an isotope of one element is at the same nominal mass as an isotope of another element (e.g., Mo 98 and Ru 98, or Se 82 and Kr 82). Corrections for isobaric interferences may be made by measuring the intensity due to the interfering element at another isotope and using its natural abundance ratios to correct for its presence at the analytical mass of interest. Most commonly used corrections for isobaric interferences are already present as default interference equations in the ELAN® Version 3.4 software. Care should be taken that the isotope measured for correction purposes does not suffer from overlap with other isotopes that may be present in the sample.

3.2. Molecular interferences are caused by molecular species formed in the plasma with plasma or matrix ions (examples of common molecular interferences include ArCl, ClO, Nitrogen dimer, oxygen dimer, oxide species, double charged species, etc.) Predictions about the type of molecular interferences may be made using knowledge about the sample matrix. Molecular interferences can often be corrected for in the same manner as isobaric interferences, i.e., measuring the intensity present at another isotope and using isotope ratios to calculate the amount of the interfering species. For example, corrections for interferences of $Ar_{40}Cl_{35}$ on As at mass 75 may be made by measuring the intensity of ArCl present at mass 77 ($Ar_{40}Cl_{37}$) and converting to the apparent intensity of ArCl at mass 75 by using the isotopic ratio of Cl_{37} to Cl_{35}. Method 200.8 requires the use of several such corrections.

3.3. A list of the interferences and corrections used is given in the listing of the isotopes monitored in Table 1.

3.4. Standards and samples are matrix matched to minimize the interferences from HCl on quantitated values.

4. Safety

Laboratory safety practices addressed on the laboratory's safety manual should be followed at all times.

4.1. Protective Equipment

4.1.1. The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory technique and safety practices should be followed at all times.

4.1.2. Safety precautions must be taken when handling acids, reagents and samples. Protective clothing including lab coats, safety glasses and gloves should be worn. Contact lenses must not be worn.

4.1.3. Acid spill kits are located under the sink in the metals prep laboratory.

4.1.4. The ELAN® 9000 is fully interlocked to protect the user from dangers such as high voltages, radio frequency generators, and intense ultra-violet light. At no time should the operator attempt to disable these interlocks or operate the ELAN® 9000 if any safety interlock is known to be disabled or malfunctioning.

4.2. Chemicals

4.2.1. Liquid argon represents a potential cryogenic hazard and safe handling procedures should be used at all times when handling liquid argon tanks.

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Freedom_0006095_0487

4.2.2. Spilled samples, reagents, and water should be cleaned up from instrument and autosampler surfaces immediately.

4.2.3. If solutions come into contact with your eyes, flush with cold water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water.

4.2.4. All spills should be reported to the program manager as soon as possible.

4.2.5. MSDS sheets are located in the metals laboratory inside the Material Safety Data Sheet binder located by the balance room.

5. Sample Handling

5.1. Sample Collection

5.1.1. Samples are collected in 1L cleaned plastic jugs. Jugs are supplied by the lab to the customer.

5.2. Sample Preservation

5.2.1. For the determination of total recoverable analytes in aqueous samples, samples are not filtered, but acidified with nitric acid to pH <2 (normally, 2 mL of acid per liter of sample is sufficient for most drinking water samples). Preservation may be done at the time of collection; however, to avoid the hazards of strong acids in the field, transportation restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within 14 days of collection and acid preserved upon receipt in the laboratory.

5.2.2. Following acidification, the sample must be mixed, held for 16 hours, and then verified to have a pH <2 If the sample pH is >2, add 2 mL nitric acid and hold for an additional 16 hours until verified to be pH <2.

5.3. Preservation Verification

5.3.1. Field sample pH verification is done in the laboratory using narrow range pH paper.

5.3.2. Withdraw an aliquot of sample to measure pH. The analyst should avoid placing the pH paper directly into the sample bottle.

5.4. Sample Storage

5.4.1. Samples can be stored for 6 months after preservation with a pH <2.

5.5. Sample Rejection

5.5.1. Any regulatory compliance monitoring sample may be rejected for any of the specific reasons listed below that are not covered in the Quality Assurance Manual.

5.5.1.1. Sample > 14 days old when received in the laboratory

5.5.1.2. Sample was collected in a bottle not provided/ approved by the laboratory.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0488

5.5.1.3. Sample volume was less than 1 liter.

6. Equipment and Supplies

6.1. Equipment

6.1.1. Perkin-Elmer ELAN® 9000 ICP-MS - Includes ELAN® 9000 instrument, computer system, ELAN® Version 3.4 software, printer, Perkin-Elmer S-10 Autosampler, and Polyscience Whispercool chiller.

6.1.2. Mechanical Pipets- varying sizes 10, 20, 100, 200 and 1000 µl with metals free tips. Calibrated annually.

6.1.3. DigiPREP Jr. sample digester with Class A volumetric digestion tubes.

6.1.4. Sonicator

6.2. Supplies

6.2.1. 1-liter plastic sample container.

6.2.2. 50mL digestion tubes and 35 mL metals free centrifuge tubes.

6.2.3. 50mL and 15mL Autosampler tubes.

6.2.4. Volumetric Flask- Class A Polymethylpentane(PMP), varying sizes 100 and 1000mL.

6.2.5. Peristaltic Pump Tubing

6.2.5.1. Black/White, (for spray chamber and rinse station drain) 0.125 inch ID. INT STD?

6.2.5.2. Black/Black, (for sample introduction, and rinse station supply) 0.030 inch ID.

6.2.6. pH paper- for testing the preservation of samples.

6.2.7. 10 mL PTFE beakers

6.2.8. 0.45µm PTFE filter disc with lurlock syringe.

7. Reagents and Standards

All solutions must be recorded in the Metals Standards and Reagents Tracking Log.
A Certificate-of-Analysis must be kept on file for all reagents, standards, and quality controls.

All reagents may contain impurities that may affect the integrity of the analytical results. Due to the high sensitivity of ICP-MS, high-purity reagents, water, and acids must be used whenever possible. All acids used for this method must be of trace metals grade or better. Nitric acid is preferred for ICP-MS in order to minimize polyatomic interferences. It should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for polyatomic ion interferences

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0489

must be used. All quality controls solutions are matrix matched with digested samples to mimic the interferences of HCl.

7.1. Reagents

7.1.1. Liquid Argon, or Ultra High Purity Argon Gas, 99.95%

7.1.2. Nitric acid, concentrated. Ultra-pure from sub-boiling distillation is preferred, but in many instances trace metals grade will suffice as long as it is free of analytes of interest. Acid(s) is deemed metals free daily by the analysis of laboratory blanks prepared with the acid(s) used.

7.1.3. Hydrochloric acid, concentrated. Ultra-pure from sub-boiling distillation is preferred, but in many instances trace metals grade will suffice as long as it is free of analytes of interest. Acid(s) is deemed metals free daily by the analysis of laboratory blanks prepared with the acid(s) used.

7.1.4. Reagent water equivalent to ASTM Type I water (≥18.0 megohms). Reagent water is currently produced using a US Filter Plus 150 Service Deionization unit followed by a Barnstead Easypure II polisher.

7.1.5. Single element stock standards – 1000 mg/L of each of the following elements: Ca, Cd, Fe, Na, Mg, Mn Se and Zn. These are used to prepare the dual detector calibration solution. Expires according to date stamped by manufacture.

7.1.6. Stock Tuning Solution A - Single element stock standard- 10 mg/L Rh used to prepare the tuning solution. Expires according to date stamped by manufacture.

7.1.7. Stock Tuning Solution B – this is a purchased stock multi-element stock standard (VHG LMSTNG3Z-100) containing 10 mg/L of Ba, Be, Ce, Co, In, 7Li, Pb, Mg, Tb, U, and Y. Expires according to date stamped by manufacture.

7.1.8. Internal Standard Solution- this is a purchased custom blend containing 10 mg/L of Bi, In, Tb, and Y; 20 mg/L of Sc; 100 mg/L Ge, and Li6. Add 50 µL of internal standard to 50 mL of all QCs, blanks and samples after digestion and dilution of the sample digestates. Add 15µL to 15 mL aliquots of samples when using 15 mL autosampler tubes. This solution may be used after expiration date so long as the counts per second readings meet the instrument manufacturer recommendations for internal standard responses.

7.1.9. Stock Multi-element Calibration Standard (VHG SM23-100) is used to prepare calibration standards. Contains 100mg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn. Expires according to date stamped by manufacture, but may be used for an extended period of time as long as the Quality Control Sample is within limits.

7.1.10. Stock Quality Control Standard (QCS) – This is a multi-element standard obtained from a source different than the one used to prepare the calibration standard (Accustandard ICP-MS-QC2-1). This solution contains 10mg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn. The QCS is used to verify the calibration. Expires according to date stamped by manufacture.

7.2. Solutions

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Freedom_0006095_0490

7.2.1. Rinse Solution - Prepare by dispensing 20.0 mL nitric acid into a 1L PMP flask filled with 500 mL of reagent water, then fill to mark. Prepare this solution in duplicate due to the volume needed and store in a pre-cleaned 2L plastic bottle.

7.2.2. Working Tuning Solution - Contains 10 µg/L of Ba, Be, Ce, Co, In, 7Li, Pb, Mg, Rh, Tb, U, and Y. Prepare in a 1L plastic class A volumetric flask half full of D.I. water containing 10 mL of HNO_3. Add 1.0 mL of each stock tuning solution A (7.1.6) and B (7.1.7) then dilute to volume. Store in a pre-cleaned 1 L plastic bottle. Expires in 6 months.

7.2.3. Calibration Standards are prepared daily.

7.2.3.1. Calibration Blank – Prepared in a 50 mL plastic class A volumetric digestion tube by pipetting 1.0 mL of HNO3 and 0.5 mL HCL, then dilute to mark with reagent water. Next, add 50 µL of internal standard (7.1.8).

7.2.3.2. Calibration standard #1 - Containing 1 µg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn in 1% HNO_3. Prepare by pipetting 1.0 mL of calibration standard #4 (7.2.3.4) to a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube to the 50 mL mark and add 50 µL of internal standard (7.1.8). This also serves to verify the minimum reporting limit (MRL).

7.2.3.3. Calibration standard #2 - Containing 10 µg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn in 1% HNO_3.Prepare by pipetting 10µL of the stock calibration standard (7.1.9) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube and add 50 µL of internal standard (7.1.8).

7.2.3.4. Calibration standard #3 - Containing 50 µg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn in 1% HNO_3.Prepare by pipetting 50µL of the stock calibration standard (7.1.9) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube and add 50 µL of internal standard (7.1.8).

7.2.3.5. Calibration Standard #4 - Containing 100 µg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn in 1% HNO_3.Prepare by pipetting 100µL of the stock calibration standard (7.1.9) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube to the 50 mL mark and add 50 µL of internal standard (7.1.8). This standard is also used to prepare calibration standard #1.

7.2.4. Working QCS – Containing 50 µg/L of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Tl, V, Zn in 1% HNO_3.Prepare by pipetting 500µL of the stock Quality Control Standard (7.1.10) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube to the 50 mL mark and add 50 µL of internal standard (7.1.8). Prepared daily.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

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7.2.5. MRL Intermediate Solution – Containing 1.0µl Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Tl, V, and Zn in 1% HNO3. Prepared daily by pipetting 50 µl of the stock multi-element stock calibration standard (7.1.9) into a PTFE beaker containing 4.95 mL of the QC Blank (9.1.2). INF. SD

7.2.6. Sample diluent – Prepare by dispensing 20.0 mL HNO_3 and 10 mL HCl into 1 liter class A volumetric flask ½ full of reagent water. Dilute to marl and store in a 2 liter plastic bottle.

7.2.7. Dual Detector Calibration Solution- This solution contains 200 µg/L of Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, K, Mo, Ni, Pb, Sb, Tl, and V; 1 mg/L Se and Cd; 3 mg/L Ca, Fe, Mg, and Zn; 5.2 mg/L Na and Mn; 100 µg/L Bi, In, Tb (internal standards) and Y; 200 µg/L Sc (internal standard) ; 1 mg/L Ge and Li6 (internal standards) in 2% HNO_3 and 1% HCL. This solution is used to generate a calibration coefficient between the pulse and analog detectors. It is prepared by pipetting 200µL of the stock calibration standard (7.1.9), 280 µL each of 1000 mg/L stocks Ca, Fe, Mg, and Zn, 500 µL each of 100 mg/L Na and Mn, 80 µL of 1000 mg/L Se and Cd (7.1.5) and 1.0 mL of internal standard mixture (7.1.8) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube to the 50 mL mark. On occasion these concentrations may need adjusted to meet the requirements of a valid dual detector calibration. The concentrations are not a critical factor for valid calibration as long as the instrument is forced to use the analog stage of the detector by over ranging the pulse (digital) stage.

8. Initial Demonstration of Capability (IDC)

Before an analyst can analyze drinking water regulatory compliance monitoring samples an Initial Demonstration of Capability (IDC) must be completed and approved by the Program Manager.

8.1. Linear Calibration Range

Since the Linear Dynamic Range of the ICP/MS can be very large; this will not be determined by users of this SOP. Users will report concentrations determined to be less than the lowest calibration standard as "< X mg/L" where X is the concentration of the element of interest in the lowest calibration standard. Users of this SOP will dilute all samples that when initially analyzed are determined to have a concentration greater than the highest calibration standard, so that the expected concentration is within the calibration range. If there is insufficient volume of sample to make dilutions then a volume of internal standard, based on the dilution factor used, will need to be added to the diluted sample. For example, if a 10X dilution (5 mL of analyzed sample diluted to 50 mL) is performed then 0.090 mL of internal standard will need to be added to the diluted sample. The diluted sample will be reanalyzed and the new measured concentration and dilution factor will be reported.

8.2. Instrument Detection Limit (IDL)

8.2.1. At a minimum an ICV, LRB, MRL, LFB, QCS and CCC must be analyzed with each IDL study.

8.2.2. Run a QC blank (9.1) as if it were a sample for a series of 10 sequential measurements with rinsing in between each measurement.

8.2.3. Calculate the standard deviation of the 10 measurements of the blank concentration for each isotope.

8.2.4. Multiply the standard deviation by three to obtain the IDL.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

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8.2.5. The IDL must be determined whenever the following occurs: Initially as part of the Demonstration of Capability for each analyst, and after major instrument repair.

8.3. Method Detection Limit (MDL)

8.3.1. Detection limit is the minimum concentration of an analyte that can be identified with 99% confidence that the analyte concentration is greater than zero.

8.3.2. Prepare, extract and analyze at least seven replicate MRLs (9.4) over a period of at least three non-consecutive days (both extraction and analysis must be conducted over at least three days) using the procedure described in Section 11

8.3.3. Sample preservatives as described in section 5.2 must be added to these samples.

8.3.4. The method detection limit is calculated according to the following equation.

$$MDL = SD * t$$

Where:

MDL= Method Detection Limit
SD= Standard deviation for seven replicate MRL's
t= 3.14, student's *t* value for seven replicates at 99% confidence

8.3.5. The values obtained for the MDL must be greater than 0. The relative standard deviation of the seven measurements must be ≥ 10%.

8.3.6. At a minimum an ICV, LRB, MRL, QCS and CCC must be analyzed with each MDL study.

8.3.7. Determined initially when a new analyst is being qualified or after major instrument maintenance is completed.

8.3.8. A summary sheet of the MDL study must be presented to the Program Manager for review and approval. The approved data is kept on file in the Administration Area.

8.4. Initial Demonstration of Accuracy

8.4.1. The solution used in determining the method precision and accuracy is a sample matrix containing method analyte of known concentration in water, which is used to fortify reagent water of environmental samples.

8.4.2. The solution must be obtained from a source different from the laboratory calibration standards. The solution must be treated like a sample and processed through the entire analytical preparation scheme.

8.4.3. Sample preservatives must also be added to these samples

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0493

8.4.4. A Quality Control Sample is prepared at a concentration of 30µg/L. Prepare as follows: Using a 1000 mL plastic volumetric flask half full of D.I. water, add 2.0 mL of HNO_3. Pipet 3.0 mL of QCS stock standard (7.1.10) into flask and fill to mark. Store in sample bottle for 16 hrs prior to digestion.

8.4.5.This solution is digested as 4 separate aliquots as described in section 10.1.

8.4.6.The percent recovery is calculated according to the following equation:

$$R = \frac{dQCS}{QCS} \times 100$$

Where:

R= Percent Recovery
dQCS= Determined Analyte Level in QCS
QCS= Prepared Analyte Level in QCS (True Value)

8.4.7.The concentration determined for each analyte in the four QCS solutions must be within 100±10% of the stated value. If recovery of any analyte exceeds the control limit, corrective action must be taken and documented.

8.4.8.At a minimum an ICV, LRB, MRL, QCS, CCC and QC Blank must be analyzed with each study.

8.4.9.Determined initially when a new analyst is being qualified or after major instrument maintenance is completed.

8.4.10. A summary sheet of the Precision and Accuracy IDC study must be presented to the Program Manager for review and approval. The approved data is kept on file in the Administration Area.

8.5. **Initial Demonstration of Precision**

8.5.1.Using the same set of replicate data generated for Section 8.4, calculate the standard deviation and relative standard deviation of the replicate recoveries.

8.5.2.The percent relative standard deviation is calculated according to the following equation:

$$RSD = \frac{Mean}{SD} \times 100$$

Where:

RSD= Relative Standard Deviation
Mean= Average value of four analytical results
SD= Standard Deviation of four analytical results

8.5.3.The relative standard deviation (RSD) of the results of the replicate analyses must be ≤ 20%. If RSD of the analyte exceeds the acceptance limit, corrective action must be taken and documented.

8.5.4.Determined initially when a new analyst is being qualified or after major instrument maintenance is completed.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0494

8.5.5. A summary sheet of the study must be presented to the Program Manager for review and approval. The approved data is kept on file in the Administration Area.

8.6. **Analysis of an Unknown**

8.6.1. The determination of the unknown sample demonstrates the analyst is capable of meeting all the requirements listed in the EPA certification manual, method specific requirements, and this standard operating procedure.

8.6.2. The unknown sample may be a drinking water proficiency testing sample or a purchased quality control sample. The true value of the quality control sample must be unknown to the analyst performing the analysis.

8.6.3. The unknown sample must be treated like a sample and prepared through the entire analytical process.

8.6.4. The control limits listed in the SOP for the Quality Control Sample (section 9.6) must be applied when calculating the percent recovery. If a drinking water proficiency testing sample is used as the unknown then the acceptance limits of the study must be applied.

8.6.5. Determined initially when a new analyst is being qualified or after major instrument maintenance is completed.

8.6.6. A summary sheet of the study must be presented to the Program Manager for review and approval. The approved data is kept on file in the Administration Area

9. Quality Controls

All unacceptable quality controls must be documented in the Corrective Action Logbook. Only the Laboratory Fortified Blank precision and accuracy values are recorded in the Quality Control Notebook.

9.1. **Quality Control Blank (QC Blank)** - is analyzed reagent water that is matrix matched to the calibration standards. The purpose of the QCBlank is to monitor instrument drift.

9.1.1. It is analyzed after the Initial Calibration Verification and Continuing Calibration Verification solutions.

9.1.2. Prepare by dispensing 1.0 mL of HNO_3 and 0.5 mL HCl into a 50 mL digestion tube half full reagent water and fill to mark. Next, add 50 µL of internal standard (7.1.8).

9.1.3. Corrective action should be taken and documented if the value exceeds the MRL. Repeat and upon second consecutive failure, recalibrate instrument and reanalyze all samples and any affected quality controls after the last passing QC Blank. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

Note: The method limit for the blank is <MDL. Because this SOP and analysis does not report down to the MDL but to the lowest calibration standard(MRL), the criteria used and approved by

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Freedom_0006095_0495

EPA Region III auditors is <MRL. Failed QC Blanks must be documented in the Method 200.8 QC and Corrective Action Logbook.

9.2. **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, sample preservatives, and internal standards that are used in the extraction batch. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

9.2.1. An LRB is required with each extraction batch of 20 samples to determine the background system contamination.

9.2.2. The solution must be treated like a sample and processed through the entire analytical preparation scheme, including sample bottles and sample digestion. Add 2mL of HNO_3 to a 1L sample bottle. This solution must be held for 16 hours after acidification prior to digestion.

9.2.3. Prepare by dispensing 1.0 mL of HNO_3 and 0.5 mL HCl into a 50 mL digestion tube and fill to the 50 mL mark with the solution described in section 9.2.2.

9.2.4. LRB values must be less than the MRL, if this limit is exceeded then fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been identified, corrected, and verified with acceptable LRB performance.

Note: The method limit for the LRB is <MDL. Because this SOP and analysis does not report down to the MDL but to the lowest calibration standard(MRL), the criteria used and approved by EPA Region III auditors is <MRL.

9.2.5. When LRB values constitute 10% or more of the analyte level determined for a sample, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been identified, corrected, and verified with acceptable LRB performance. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.3. **Laboratory Fortified Blank (LFB)** – An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

9.3.1. An LFB is required with each extraction batch of 20 samples to determine the background system contamination.

9.3.2. The solution must be treated like a sample and processed through the entire analytical preparation scheme, including sample bottles and sample digestion.

9.3.3. Prepare by dispensing 1000µL of HNO_3, 500µL HCl, and 10µL of the Stock Calibration Standard (section 7.1.9) into a 50 mL digestion tube and fill to mark with the LRB solution (9.2.2).

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0496

9.3.4.The percent recovery is calculated according to the following equation:

$$R = \frac{LFB - LRB}{S} * 100$$

Where:

R = Percent Recovery
LFB = Lab Fortified Blank Result
LRB = Lab Reagent Blank Result
S = amount of spike added (in concentration units)

9.3.5.The percent recovery for the LFB must be within the required control limits of 85-115%. If the recovery is not in control, the source of the problem should be identified and resolved before analysis is continued. Document percent recovery and any erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.3.6.The results from the LFB must be graphed and kept on file for review.

9.4. **Minimum Report Limit (MRL)** - is the minimum concentration that can be reported by a laboratory as a quantified value for the method analyte in a sample following analysis.

9.4.1.An MRL is required daily with each analytical run.

9.4.2.The solution must be treated like a sample and processed through the entire analytical preparation scheme, including sample bottles and sample digestion.

9.4.3.Prepare by dispensing 1000µL of HNO_3, 500µL HCl, and 50µL of the MRL Intermediate solution (7.2.5) into a 50 mL digestion tube and fill to mark with the LRB solution.

9.4.4.To prepare the MRL solution for Aluminum, prepare as above (9.4.3) except use 500 µL of MRL Intermediate solution (7.2.5).

9.4.5.The percent recovery is calculated according to the following equation:

$$R = \frac{MRL - LRB}{S} * 100$$

Where:

R = Percent Recovery
MRL = Minimum Reporting Limit Result
LRB = Laboratory Reagent Blank Result
S = amount of spike added (in concentration units)

9.4.6.The percent recovery for the MRL must be within the required control limits of 50-150%. If the recovery is not in control, the source of the problem should be identified and resolved before analysis is continued. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.5. **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of a Field Sample to which known quantities of the method analytes and all the preservation compounds are added. The LFM is processed and analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0497

The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

9.5.1.The laboratory must spike a known amount of analyte into a minimum of 10% of all samples.

9.5.2.The solution must be treated like a sample and processed through the entire analytical preparation scheme, including sample bottles and sample digestion.

9.5.3.The aliquot used for the LFM must be a duplicate of the aliquot used for sample analysis and the added analyte concentration must be the same as that used in the Laboratory Fortified Blank (LFB).

9.5.4.Prepare by dispensing 1000µL of HNO_3, 500µL HCl, and 10µL of the Stock Calibration Standard (7.1.9) into a 50 mL digestion tube and fill to mark with sample.

9.5.5. The percent recovery is calculated according to the following equation:

$$R = \frac{C_S - C}{S} * 100$$

Where:

R = Percent Recovery
C_s = Measured concentration in fortified sample matrix
C = Measured concentration in unfortified sample
S= Amount of analyte added to sample matrix

9.5.6.The recovery of the LFM must be within the designated acceptance range of 70-130%. If it is not within this range, and the LFB recovery is acceptable, the data user should be informed that the result in the unfortified sample is suspect due to heterogeneity or an uncorrected interference effect.

Note: Recovery calculations are not required if the concentration of the analyte added is less than 30% of that present in the sample.

9.6. **Quality Control Sample (QCS)** - A sample that is obtained from a source external to the laboratory and different from the source of calibration standards. The QCS is used to check calibration standard integrity.

9.6.1.A QCS is required daily with each analytical run.

9.6.2.The QCS is prepared according to section 7.2.4.

9.6.3.The percent recovery is calculated according to the following equation:

$$R = \frac{dQCS}{QCS} \times 100$$

Where:

R= Percent Recovery
dQCS= Determined Analyte Level in QCS
QCS= Prepared Analyte Level in QCS (True Value)

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0498

9.6.4. The QCS results must be within 100±10% of the stated value. If the QCS is not within these limits, an immediate second analysis should be performed to confirm unacceptable performance. If the second analysis result is unacceptable, the analysis should be terminated and the source of the problem identified, and corrected before continuing. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.7. **Initial Calibration Verification (ICV)** - A calibration standard containing the method analytes, internal standard(s) and surrogate(s), which is analyzed initially to verify the accuracy of the existing calibration for those analytes.

9.7.1. The initial calibration verification (ICV) is performed by analysis of the mid-calibration standard (50µg/L) immediately following the calibration routine.

9.7.2. Prepare by pipetting 50µL of the stock calibration standard (7.1.9) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube and add 50 µL of internal standard.

9.7.3. The percent recovery is calculated according to the following equation:

$$R = \frac{ICV}{IC} \times 100$$

Where:

R= Percent Recovery
ICV= Analyte Level Determined from the ICV
IC= Prepared Analyte Level in the Calibration Solution(50µg/L)

9.7.4. The results determined for each analyte at each level must be within 100±10% of calibration. If the calibration can not be verified within the specified limits, repeat the analysis. Upon second failure the instrument must be recalibrated. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.8. **Continuing Calibration Verification (CCV)** - A calibration standard containing the method analytes, internal standard(s) and surrogate(s), which is analyzed periodically to verify the accuracy of the existing calibration for those analytes.

9.8.1. The continuing calibration verification (CCV) is performed by analysis of the mid-calibration standard (50µg/L) after every ten field samples and at the end of the run.

9.8.2. Prepare by pipetting 50µL of the stock calibration standard (7.1.9) into a 100 mL plastic class A volumetric flask half full of D.I. water containing 2.0 mL of HNO_3 and 1.0 mL HCl, then dilute to mark. Dispense into a 50 mL digestion tube and add 50 µL of internal standard.

9.8.3. The percent recovery is calculated according to the following equation:

$$R = \frac{CCV}{IC} \times 100$$

Where:

R= Percent Recovery
CCV= Analyte Level Determined from the CCV run

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0499

IC= Prepared Analyte Level in the Calibration Solution (50µg/L)

9.8.4. If the continuing calibration verification is not confirmed within ±15% of calibration, the previous 10 samples must be reanalyzed after recalibration. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.9. **Internal Standard (IS)** - A pure analyte added to an extract or standard solution in a known amount and used to measure the relative responses of other method analytes and surrogates. The internal standard must be an analyte that is not a sample component.

9.9.1. The internal standard must be added to all samples, calibration standards, blanks, and quality controls.

9.9.2. The internal standard intensities should be monitored throughout the sample set being analyzed. Ratios of the internal standard intensities against each other should also be monitored routinely. This information can be used to detect potential problems caused by mass dependent drift, internal standard addition errors and increases in internal standard concentrations due to background contributions.

9.9.3. The percent recovery is calculated according to the following equation:

$$R = \frac{CISR}{IISR} \times 100$$

Where:

R= Percent Recovery
CISR= Current Internal Standard Response
IISR= Initial Internal Standard Response in the Calibration Blank

9.9.4. The intensities of the internal standards must be within 60-125% of the original response in the calibration standard blank.

9.9.4.1. If the responses are not within the above limits, flush the system with the calibration blank (7.2.3.1) and monitor the intensities of the internal standards in the calibration blank.

9.9.4.2. If the intensities are now within the limits, take a fresh aliquot of the sample and dilute by a factor of two and add appropriate internal standards and reanalyze.

9.9.4.3. If the intensities in the calibration blank are not within the limits, terminate the analyses, determine and correct the source of the problem. Document any erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.10. **Duplicated (DUP)** - A second aliquot of the Field Sample analyzed identically to the initial field sample. The duplicate is used to access method precision and accuracy when the occurrence of a target analyte is infrequent.

9.10.1. Within each extraction batch, of 20 field samples a minimum of one Duplicate or Laboratory Fortified Sample Matrix Duplicate (LFMD) must be analyzed. Analytes analyzed by this SOP are typically found in drinking water; however, if target analytes are not routinely observed in Field Samples, an LFMD should be analyzed rather than a Laboratory Duplicate.

4710 Chimney Drive Suite G, Charleston WV 25302 Phone (304)965-2694 Fax (304)965-2696

Freedom_0006095_0500

9.10.2. The solution must be treated like a sample and processed through the entire analytical preparation scheme, including sample digestion.

9.10.2.1. **Laboratory Fortified Sample Matrix Duplicate (LFMD)**

9.10.2.1.1. The aliquot used for the LFMD must be a duplicate of the aliquot used for sample analysis and the added analyte concentration must be the same as that used in the Laboratory Fortified Blank (LFB).

9.10.2.1.2. Prepare by dispensing 1000µL of HNO_3, 500µL HCl, and 10µL of the Stock Calibration Standard (7.1.9) into a 50 mL digestion tube and fill to mark with sample. Next, add 50 µL of internal standard (7.1.8)

9.10.2.2. **Laboratory Duplicate (LD)**

9.10.2.2.1. The aliquot used for the LD must be a duplicate of the aliquot used for sample analysis.

9.10.2.2.2. Prepare by dispensing 50 mL of preserved sample (5.2) into a 50 mL digestion tube and add 1000 µL of HNO_3 and 500 µL HCL. Next, add 50 µL of internal standard (7.1.8)

9.10.3. The relative percent difference is calculated according to the following equation:

$$RPD = \frac{RA - RB}{((RA - RB)/2)} \times 100$$

Where:

RPD = Relative Percent Difference
RA = Response from initial analysis
RB = Response from second analysis

9.10.4. Relative percent difference must be ≤10%. If the relative percent difference exceeds control limits corrective action must be taken to correct the lack of instrument precision and or/preparation consistency. Calibration standards and sample must be reanalyzed if results are exceeded on second analysis or take other appropriate corrective action. Document erroneous results in the Method 200.8 QC and Corrective Action Logbook.

9.11. **CORRECTIVE ACTION LOG BOOK** - When a result is outside the acceptable limits established for a quality control parameter the resulting failure must be documented in the Corrective Action Logbook.

10. Procedure

10.1. **Sample Digestion** – All samples analyzed by this SOP are digested and reported as total recoverable metals.

10.1.1. All digestion must be recorded in the Digestion Notebook.

10.1.2. All field samples along with the LRB, MRL, LFB, DD, LFM, and LFMD are digested according to the following procedure.

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Freedom_0006095_0501

10.1.3. Place a digital thermometer in a temperature control blank for each heating block in use. The reagent water should be at the same level as the samples.

10.1.4. Prepare all field samples by dispensing 50 mL of preserved sample (5.2) into a 50 mL digestion tube and add 1000 µL of HNO_3 and 500 µL HCL. 2% 1%

10.1.5. Place all field samples and quality controls in the digestion block and cover, heat at 85°C. Apply heat until liquid has evaporated to 1/5th the original volume, then cap and reflux for 30 min.

?

10.1.5.1. If a significant amount of solids are not dissolved after digestion, the prepared digestate is filtered though a 0.45µm PTFE filter disc prior to analysis to prevent clogging of the nebulizer. Results will be reported as dissolved metals and not total recoverable metals.

10.1.5.2. The LRB, MRL, and LFB must be processed in the same manner to ensure no interferences are present in the filter.

10.1.6. Allow to cool and fill to 50 mL mark with reagent water.

no dilution ?

10.1.7. Transfer an aliquot of the digested sample to a 15 mL Autosampler tube. Next, add the internal standard (7.1.8) at a ratio of 1µl internal standard per 1mL of sample.

10.2. **Instrument Startup**

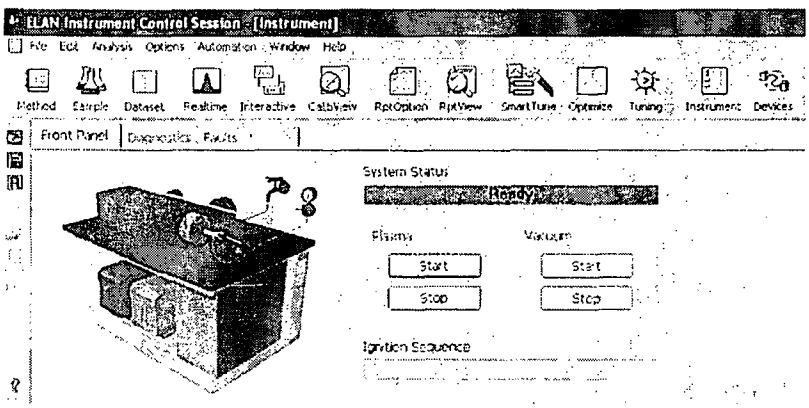
10.2.1. Ensure that all circuit breakers on the left side of the Perkin Elmer Elan 6000 are in the On position. If they are not, allow five seconds before turning on each breaker in the following sequence 1) 2) 3) and 4).

10.2.2. Turn on the ICP-MS chiller using the front upper-right rocker switch.

10.2.3. Verify that there is sufficient argon for the analysis and the pressure is set at 60 psi.

10.2.4. Engage the compression cams on the integrated peristaltic pump located on the instrument and Autosampler to secure the drain and sample tubing.

10.2.5. Make sure the instrument exhaust fume hoods are on and operational. The on/off switch is located on the right of the instrument and labeled "ICP".



10.2.6. Turn on the IBM desktop computer system. Move the mouse pointer to the ***ELAN SHORTCUT*** icon and double click. This will open the ELAN software main page.

10.2.7. Click on the **INSTRUMENT BUTTON** and then click the **FRONT PANEL TAB.** The *SYSTEM STATUS* indicator should read ***READY*** if all system hardware is operating properly.

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Freedom_0006095_0502

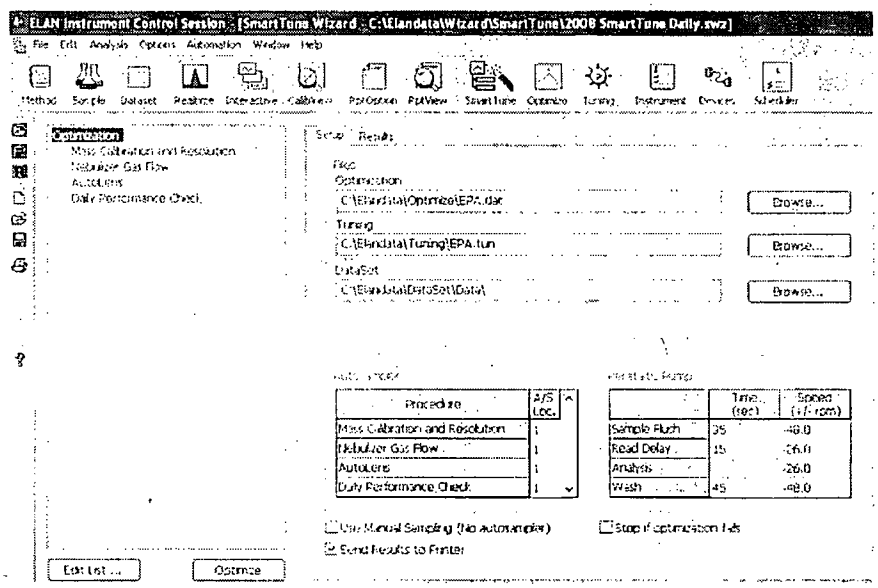
10.2.8. Ensure the finish vacuum pump is operational and running. When satisfactory vacuum (10-6 torr) has been achieved, the vacuum chamber in the schematic diagram turns green. In the event that the finished pump is turn off it can turned on by clicking the **VACUUM START BUTTON**.

10.2.9. Perform a visual check of the sample introduction system and ensure it is in working order. This should include the autosampler, pump tubing, spray chamber, torch, sample cones and pump oils.

10.2.10. Next, ignite the plasma by clicking on the **PLASMA START BUTTON**. Allowed ICP/MS to warm up for approximately 30 minutes.

10.3. **Tuning and Optimizing System**

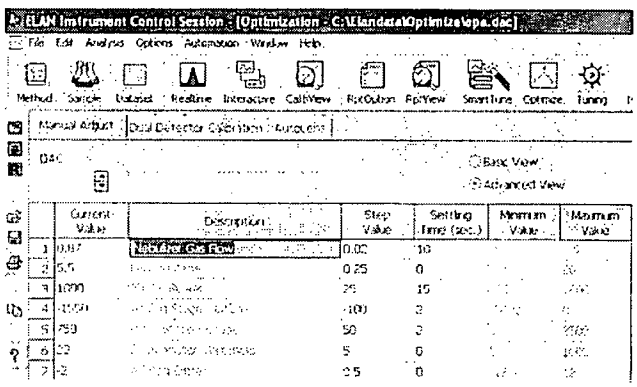
10.3.1. Click on the **SMARTTUNE BUTTON** to open the **2008 SmartTune Daily.swz** workspace. If this workspace does not open, click on *FILE* then *OPEN* and select it from the listing. The specs for the wizard are outlined in Appendix E.



This wizard automatically tunes the Mass Spectrometer, and optimizes the Nebulizer Gas Flow, and the Auto Lens Voltage. The wizard concludes by running a daily performance check. The analysis of the daily performance solution must meet the criteria listed in Appendix D. Additionally, the %RSD for the analytes in the five replicates run during the daily performance check need to be reviewed to ensure that they are less than 5%. If any of the performance levels listed in Appendix D or the %RSD for the replicates are not met then the corrective actions listed in the software guide must be taken.

10.3.2. Place a 50 mL auto sampler tube filled with the Working Tune Solution (7.2.2) into autosampler position one.

10.3.3. Click on the **SMARTTUNE OPTIMIZATION BUTTON** to run the daily tune wizard. While the instrument runs the daily tune wizard the result can be reviewed by clicking on the **SMARTTUNE RESULTS TAB**.



10.3.4. After the completion of the daily tune wizard, the TUNE and OPTIMIZATION files must be saved if all the conditions listed in table 3 are acceptable. See the corrective actions listed in the software guide to resolve any issues.

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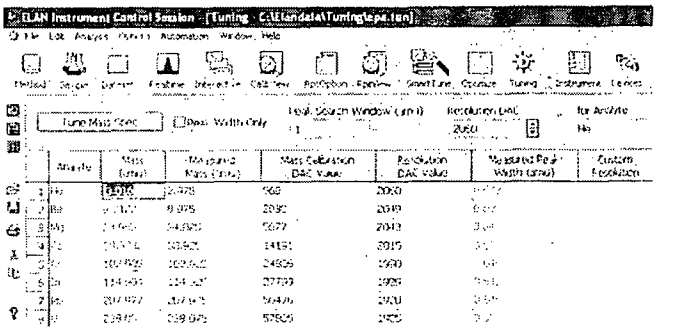
Freedom_0006095_0503

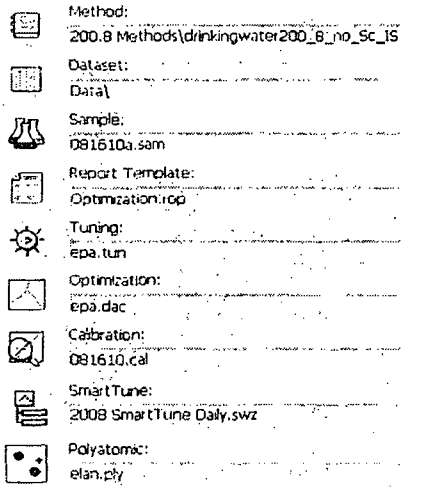
10.3.5. To save the optimization data, first click on the **OPTIMIZATION BUTTON** to open the optimization main window. Next, click on *FILE* then *SAVE*, the optimization data will be saved in the file **EPA.DAC.**



10.3.6. To save the tuning data, first click on the **TUNING BUTTON** to open the optimization main window. Next, click on *FILE* then *SAVE*, the tuning data will be saved in the file **EPA.TUN.**

10.4. Performing Routing Analyses

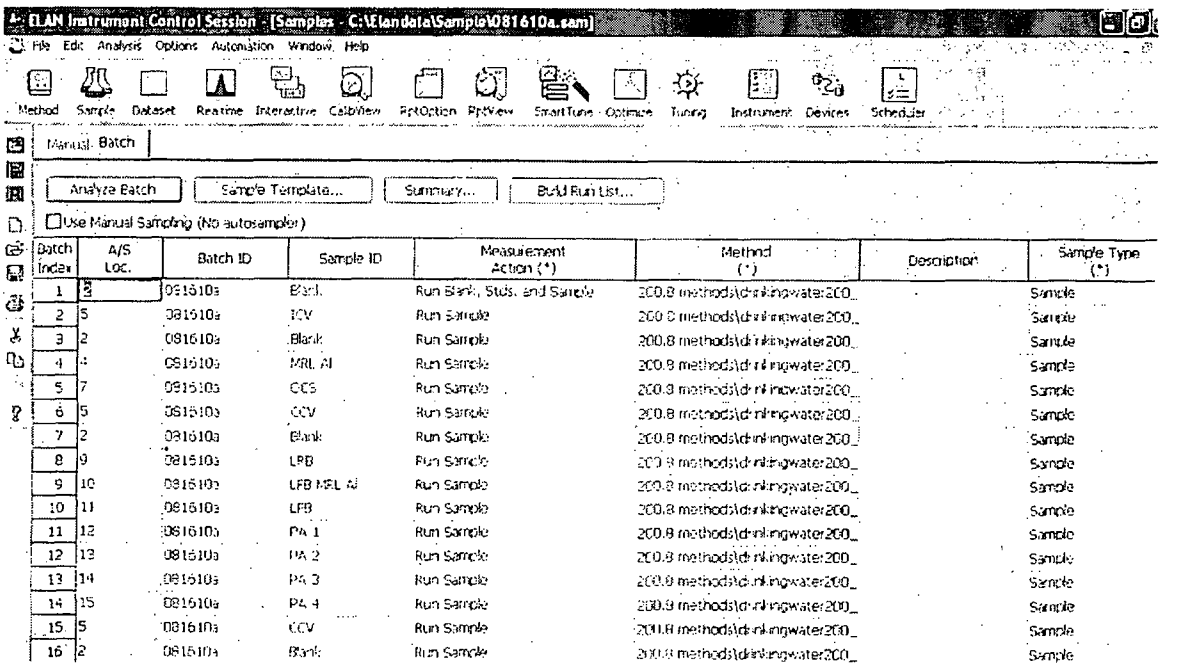
10.4.1. The analyst must identify the samples, quality controls and the order in which they are measured. The sample window serves as the principle interface to control the sample introduction during an analysis.



10.4.2. To start the process, click on *FILE* and *OPEN WORKSPACE*, next select **DRINKINGWATER200_8USETHIS.wrk.** To review the workspace data, click on the letter **R** located on the left side of the console.

10.4.3. Ensure the following parameters are correctly defined in the workspace.

Method:	**DRINKINGWATER200_8_NO_SC_IS.MTH**
Tuning:	**EPA.TUN**
Optimization:	**EPA.DAC**
SmartTune:	**2008 SMARTTUNE DAILY.SWZ**
Dataset:	**C:\ELANDATA\DATASET\DATA**



Batch Index	A/S Loc.	Batch ID	Sample ID	Measurement Action (*)	Method (*)	Description	Sample Type (*)
1	3	081610a	Blank	Run Blank, Stds, and Sample	200.8 methods\drinkingwater200_		Sample
2	5	081610a	ICV	Run Sample	200.8 methods\drinkingwater200_		Sample
3	2	081610a	Blank	Run Sample	200.8 methods\drinkingwater200_		Sample
4	4	081610a	MRL Al	Run Sample	200.8 methods\drinkingwater200_		Sample
5	7	081610a	CCS	Run Sample	200.8 methods\drinkingwater200_		Sample
6	5	081610a	CCV	Run Sample	200.8 methods\drinkingwater200_		Sample
7	2	081610a	Blank	Run Sample	200.8 methods\drinkingwater200_		Sample
8	9	081610a	LFB	Run Sample	200.8 methods\drinkingwater200_		Sample
9	10	081610a	LFB MRL Al	Run Sample	200.8 methods\drinkingwater200_		Sample
10	11	081610a	LFB	Run Sample	200.8 methods\drinkingwater200_		Sample
11	12	081610a	PA 1	Run Sample	200.8 methods\drinkingwater200_		Sample
12	13	081610a	PA 2	Run Sample	200.8 methods\drinkingwater200_		Sample
13	14	081610a	PA 3	Run Sample	200.8 methods\drinkingwater200_		Sample
14	15	081610a	PA 4	Run Sample	200.8 methods\drinkingwater200_		Sample
15	5	081610a	CCV	Run Sample	200.8 methods\drinkingwater200_		Sample
16	2	081610a	Blank	Run Sample	200.8 methods\drinkingwater200_		Sample

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Freedom_0006095_0504

10.4.4. Next click the **SAMPLE BUTTON** to open the run schedule to populate it with the calibration standards, samples, and quality controls.

10.4.5. The first column ***A/S Loc.*** defines the location of each sample and quality control. Enter the number corresponding to the position in the autosampler tray where the sample solution will be placed.

10.4.6. The ***Batch ID*** identifies a group of samples with a batch label. The date of analysis is entered as the batch ID name and in this format MMDDYY, where MM = Month, DD = Day, and YY = Year.

10.4.7. Under the heading ***Sample ID,*** start with enter the description of each quality control; ICV, QC Blank, LRB, MRL, LFB, and QCS. Next enter all sample laboratory numbers and any required quality controls.

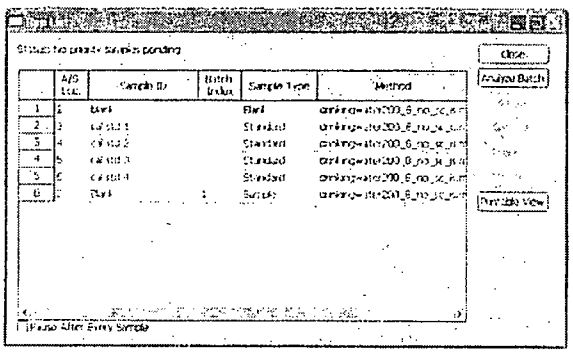
10.4.8. ***Measurement Action*** specifies when to run standard and blank solutions, in addition to specifying the running of the sample solution. To select a calibration action, right-click the appropriate cell of the Samples data table to open the drop-down menu and click the desired Measurement Action. Several measurement actions are available to choose from. Select RUN BLANK, STD, and SAMPLE for the first row. This will result in the calibration curve being analyzed followed by the first solution listed in row one. All samples and quality controls will have measurement action RUN SAMPLE selected.

10.4.9. The ***Method*** column specifies the method to be used for measuring the related sample solution and for all following samples. Right-click on the cells underneath this column and select the following method for all **DRINKINGWATER200_8_NO_SC_IS.MTH**

10.4.10. ***Sample Type*** identifies samples being used for a quality control determination. Several options are available to choose form. Right-click the Sample Type field and select SAMPLE for all.

10.4.11. Next the run schedule must be saved, click on *FILE* and *SAVE*, enter the name used for the field BATCH ID.

10.4.12. To select all the items to be analyzed, left click on the first row and drag the pointer to the last row in the run schedule just created. All items just selected should be highlighted. Next click the **BUILD RUN LIST BUTTOM**, the run list window will appear.



10.4.13. The run schedule must be printed with each analyses batch. To print the highlight items selected to be analyzed, click on the **PRINTABLE VIEW**.

10.4.14. To begin the analysis run click **ANALYZE BACH BUTTON** to start analyses.

11. Data Analysis and Calculations

11.1. Data Analysis

11.1.1. All calculations necessary to convert raw data (ion counts/second) are performed by the ELAN® software. The calculated quantities are selected by choosing the desired options in the Report Options

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screen. The default report option for this method is QuantSum.rop. If the user desires, this format can be edited and saved under a new name.

11.1.2. The analyte isotopes monitored are listed in Appendix A. When more than one isotope is monitored the primary isotope for analytical determination is underlined. Additionally, the internal standards associated with each grouping of analytes are listed.

11.1.2.1. If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible interferences. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

11.1.3. All calculations performed in the ELAN® software are based on the ratio of the analyte intensity (cps) to the internal standard intensity (cps). In all calculations where internal standards are used (Method 200.8 requires the use of internal standards) the ratio of the analyte intensity to internal standard intensity is taken before any other calculation is performed.

11.1.4. Quality Control Sample, Continuing Calibration Verification, and Internal Standard results may be checked using the QC Checking features in the ELAN® software. All values entered in the method should be checked and edited to match the true values used for the specific analysis.

11.1.5. Report only those values that fall between the lowest and highest calibration standards. Samples that exceeded the highest calibration standard must be diluted into range and reanalyzed. Diluted samples result must have the correct dilution factor applied before reporting.

11.1.6. Report results using the correct number of significant figures(3).

11.1.7. When a sample is analyzed in duplicate the initial result is reported and the second result is for the determination of method precision only.

11.1.8. Samples that are below the lowest calibration standard are reported as: < Minimum Reporting Limit.

11.1.9. Results that exceed the Environmental Protection Agency Maximum Contaminant Level must be reported within 24 hours to the Bureau for Public Health Office of Environmental Health Services Data Management Group.

11.2. Calculations

11.2.1. The calibration curve type used within this SOP is linear regression. The calibration curve correlation coefficient must be ≥0.995. If the condition is not met then corrective action must be taken and documented, such as.

11.2.1.1. Fresh calibration standards.
11.2.1.2. Prepare new stock solutions.
11.2.1.3. Calibrate mechanical pipettes.
11.2.1.4. Instrument Maintenance.

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11.2.2. For the total recoverable analytes preparation procedure, the concentrations for As and Se are calculated using the following equation. See section 9.6. All other analytes can be reported without this dilution unless a dilution is needed to bring the analyte concentration within the calibration range.

$$Sample\ Concentration = \frac{C \times V_F}{V_I}$$

Where:

C = Measured Concentration (µg/L)
V_F = Final Volume of Sample (0.015 L)
V_I = Initial Volume of Digestate (0.006 L)

Note: The dilution of the digestate required for the removal of chloride interference, results in a dilution factor of 2.5 that is applied to the measured concentration.

12. Troubleshooting and Maintenance

12.1. Many problems can occur when using this instrument, for detailed explanation of causes and troubleshooting refer to the instrument software guide and the training manual listed in the references.

12.2. Maintenance log sheets should be filled out daily and on an as needed basis. Retain the log sheets for the duration of the instrument. Trends of various parameters can be an indicator of the condition of the instrument.

12.3. Daily Performance data, routine and non-routine maintenance are documented in the Instrument Logbook.

12.4. The ELAN data set has a 2000 entry file limit, and when full it will not capture data. Copy the files to another location prior to deleting.

13. References

13.1. "Method 200.8 Determination of Trace Element in Waters and Waste by Inductively Coupled Plasma-Mass Spectrometry", Rev. 5.4 (1994), J.T. Creed, C.A. Brockoff, and T.D. Martin, U.S. Environmental Protection Agency.

13.2. EPA 815-R-05-004 "Manual for the Certification of Laboratories Analyzing Drinking Water: Criteria and Procedures, Quality Assurance", Fifth Edition, January 2005,U.S. Environmental Protection Agency.

13.3. ELAN Version 3.4 ICP-MS Software Guide, 2007, Perkin-Elmer Corporation.

13.4. ELAN 9000 Hardware Guide, 2005, Perkin-Elmer Corporation.

13.5. "ICP-MS Customer Training Course" Manual, Rev.C, Perkin-Elmer Corporation.

13.6. "West Virginia Department of Health and Human Resources Office of Laboratory Services Manual of Quality Assurance", 2009

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13.7. "Operation of the Perkin Elmer Elan 6100 ICP-MS" SOP, EPA Region 3, Office of Analytical Services and Quality Assurance, document number R3QA116

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Freedom_0006095_0508

APPENDIX A - Quality Control Limits and Corrective Action Summary

Quality Control Type	Limits	Frequency
Quality Control Sample (QCS)	100 ± 10% Rec.	Each Run
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause. If found necessary prepare and new QCS.		
Laboratory Reagent Blank (LRB)	< MRL or < 10 sample analyte	Each Digested Batch of 20 field samples or fewer
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine source of contamination and eliminate. Re-digest samples associated with the unacceptable LRB		
Laboratory Fortified Blank (LFB)	100 ± 15% Rec.	Each Digested Batch of 20 field samples or fewer
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause of analyte lose or source of contamination and eliminate. Re-digest samples associated with the unacceptable LFB		
Minimum Reporting Limit (MRL)	100 ± 50% Rec.	Each Run
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause. If the MRL fails often, consider raising the concentration. Re-digest samples associated with the unacceptable MRL.		
Initial Calibration Verification (ICV)	100 ± 10% Rec.	Immediately after the calibration curve
Corrective Action: Repeat until second failure. Upon second failure stop analysis and recalibrate instrument.		
Continuing Calibration Verification (CCV)	100 ± 15% Rec.	Every 10th sample and end of run
Corrective Action: Repeat until second failure. Upon second failure stop analysis and recalibrate instrument and reanalyze all samples back to last acceptable CCV.		
Quality Control Blank (QCBlank)	≤ MRL	After the ICV and CCV
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine source of instrument drift or contamination. Reanalyze all samples and any affected quality controls after the last passing QC Blank		
Laboratory Fortified Sample Matrix (LFM)	100 ± 30% Rec.	Each Digested Batch of 10 field samples or fewer
Corrective Action: If recovery is outside the limits and the quality controls are within limits, the recovery problem is deemed matrix related and not instrument related. The data user is notified that the result of the unfortified sample is suspect due to matrix interferences.		
Laboratory Duplicate (DUP) **Laboratory Fortified Sample Matrix Duplicate (LFMD)**	≤ 20% RPD	Each Digested Batch of 20 field samples or fewer
Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause.		
Internal Standard Response (IS)	60 – 125% Rec.	Monitored in every sample and quality control
Corrective Action: If the response is outside of these limits, flush the instrument with calibration blank and monitor the responses in the blank. If the responses are now within limits dilute the sample. If responses are not within limits, cease analysis and determine the cause of drift.		

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APPENDIX B - Table of the Isotopes Monitored, Correction Equations Used, and Potential Interferences

Analyte	Symbol	Isotopes Monitored	Correction Equations	Potential Interferences
Aluminum	Al	27		
Antimony	Sb	121, 123	Sb 123 = -0.127189*Te 125	
Arsenic	As	75	-3.127*(ArCl 77-(0.874*Se 82))	ArCl, Sm++, Nd++, Eu++
Barium	Ba	135, 137		
Beryllium	Be	9		
Cadmium	Cd	106,108, 111, 114	Cd 106= -1.223914*Pd 105 Cd 108= -1.184953*Pd105 Cd 111= -1.073*(MoO 108-(0.712*Pd 106)) Cd 114= -0.026826*Sn118	Cd 106, Pd, SrO, YO, ZrO Cd 108, Pd, MoO, ZrO Cd 111, MoO Cd 114, Sn, MoO
Chromium	Cr	52, 53		Cr, 52, ArO, SO, ArN, ClO, ArC, HClO Cr 53, HClO, HSO, ArC, ClO
Cobalt	Co	59		CaO
Copper	Cu	63, 65		Cu 63, PO2, TiO Cu 65, PO2, SO2, TiO, Ba++
Lead	Pb	206, 207, 208	Pb 208 = +1*Pb 206+1*Pb 207	
Manganese	Mn	55		HClO, ClO, ArN
Molybdenum	Mo	95,97,98	Mo 98=-0.109613*Ru 101	Ru, BrO
Nickel	Ni	60,62		Ni 60, CaO
Selenium	Se	77, 82	Se 78= -0.030461*Kr83 Se 82 = -((1.008696*Kr 83)-(0.001865*Br 81))	Se 78, Kr,Ar2,Gd++.Dy++ Se 82, Kr, Ar2H, BrH, Dy++, Ho++, Er++
Silver	Ag	107,109		Ag 107, ZrO, YO Ag 109, ZrO
Thallium	Tl	203,205		
Vanadium	V	51	-3.127*(ClO 53-(0.113*Cr 52))	ClO, HSO
Zinc	Zn	66, 67, 68		Zn 66, VO, TiO, SO2, Ba++ Zn 67, TiO, ArP, ClO2, VO, Ba++, Ba++ Zn 68, SO2, ClO2, TiO, ArS, VO, Ba++, Ce++, Ba++
Internal Standards				
Analyte	**Symbol**	**Isotopes Monitored**	**Correction Equations**	**Potential Interferences**
Lithium	Li	6		
Scandium	Sc	45		CaH, BO2, CO2, SiO, AlO, Zr++, Zr++
Germanium	Ge	72		ArS, Nd++,Sm++
Yttrium	Y	89		
Indium	In	115	-0.014032*Sn 118	Sn, MoO
Bismuth	Bi	209		

NOTE: When one more than one isotope is monitored the primary isotope for analytical determination is underlined.

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Information Only				
Analyte	**Symbol**	**Isotopes Monitored**	**Correction Equations**	**Potential Interferences**
Calcium	Ca	44		CNO, AlO, BO2, CaH, CO2, MgO, SiO, Sr++, Y++
Magnesium	Mg	24		NaH, LiO, Ca++, Ti++, Ti++
Sodium	Na	23		LiO, Ti++, Ti++, Ca++
Potassium	K	39		ArH
Iron	Fe	54	-0.028226*Cr52	Cr, HClO, ArO, ArN
Krypton	Kr	83		Er++
Ruthium	Ru	99		BrO
Palladium	Pd	105		SrO,YO
Tin	Sn	118		MoO,U++

NOTE: When one more than one isotope is monitored the primary isotope for analytical determination is underlined.

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APPENDIX C - Operating Parameters for the ELAN 9000 ICP-MS Instrument

Description	Value
Argon Line Pressure	51 psi ± 1 psi
Chiller Pressure and temperature	55 psi @ 18 °C
Nebulizer Gas Flow	0.75 to 1.2 L/min. (Optimized Daily)
Auxiliary Gas Flow	1.2 L/min.
Plasma Gas Flow	15.00 L/min.
Lens Voltage	2 to 15 V (Optimized Daily)
ICP RF Power	1100.00 W
Analog Stage Voltage	-1700 to -2500 V (Optimized Monthly)
Pulse Stage Voltage	600 to 1500 V (Optimized Monthly)
Quadrupole Rod Offset Std	0.00
Cell Rod Offset Std	-10.00
Discriminator Threshold	70.00
Cell Path Voltage Std	-15.00
RPa	0.00
RPq	0.25

APPENDIX D - Daily Performance Criteria

Parameter	Performance Level
Mass Calibration	0.05 amu
Mass Resolution	0.065 amu at 10% peak height
Nebulizer Gas Flow	Optimized for Max Rh(103) Intensity CeO/Ce ≤ 0.03
Lens Voltage	Optimized for Max Be(9), Co(59), In(115) and U(238) Intensity
Auto Lens Calibration	0.001 < Slope < 0.02
Magnesium Intensity	> 40,000 counts
Rhodium Intensity	> 150,000 counts
Indium Intensity	> 300,000 counts
Lead Intensity	> 100,000 counts
Background 220 amu Intensity	< 30 counts
Cerium Oxide Intensity / Cerium Intensity	< 3.0 %
Barium 2+ Intensity / Barium 1+ Intensity	< 3.0 %

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APPENDIX E – SmartTune Daily Wizard Settings

Mass Calibration and Resolution

Method File: C:\Elandata\Method\200.8 Methods\EPA2008 Tuning.mth

	Target Accuracy (+/- amu)	Peak Height (%)	Target Resolution (amu)	Number of Iterations
Mass Calibration	0.05			6
Resolution	0.1	10	0.65	

Target Mass list: 3.016 / 9.0122 / 23.985 / 58.9332 / 102.905 / 114.904 / 207.977 / 238.05

Nebulizer Gas Flow

Method File: C:\Elandata\Method\200.8 Methods\EPA2008 OPTIMIZE.mth

	Analyte	Operator	Analyte	Comparator	Target
Intensity	Rh 102.905			Maximum	
Formula	CeO 155.9	/	Ce 139.905	<=	0.026

Pass	Start	End	Step
Initial	0.750	1.100	0.020

AutoLens

Method File: C:\Elandata\Method\200.8 Methods\DrinkingWaterAutoLens Calibration.mth

Max Slope	0.02
Min Slope	0.001

Pass	Start	End	Step
Initial	2.000	13.000	0.250

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Final Report Results For Laboratory
West Virginia Department of Health

Ba by 200.8

2012

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ERA

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2009 TNI Evaluation Report

Study: **WS-187**

ERA Customer Number: **W213401**

Laboratory Name: **West Virginia Department of Health**

Inorganic Results

Freedom_0006095_0515

WS-187 2009 TNI Evaluation Final Complete Report

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EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID: WV00003

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
'S Hardness (cat# 555)												
1035	Calcium	mg/L	72.7	71.4	60.7 - 82.1	Acceptable	SM3500Ca D 18th ED 1992	2/17/2012	0.156	72.3	2.52	
1085	Magnesium	mg/L	20.3	19.8	16.8 - 22.8	Acceptable	SM3111B 18th ED 1992	2/22/2012	0.725	19.6	0.939	
1155	Sodium	mg/L	15.6	15.9	13.5 - 18.3	Acceptable	SM3111B 18th ED 1992	2/22/2012	-0.449	16.0	0.821	
1550	Calcium Hardness as CaCO3	mg/L	181	178	151 - 205	Acceptable	SM3500Ca D 18th ED 1992	2/17/2012	0.321	179	5.04	
1755	Total Hardness as CaCO3	mg/L	260	260	221 - 299	Acceptable	SM2340C 18th ED 1992	2/17/2012	0.0536	260	6.54	
'S Inorganics (cat# 591)												
1505	Alkalinity as CaCO3	mg/L	116	114	103 - 125	Acceptable	SM2320B 18th ED 1992	2/16/2012	0.784	112	4.43	
1575	Chloride	mg/L		81.7	69.4 - 94.0	Not Reported				80.2	2.44	
1610	Conductivity at 25°C	µmhos/cm	650	659	593 - 725	Acceptable	SM2510B 18th ED 1992	3/16/2012	-1.62	675	15.3	
1730	Fluoride	mg/L	3.92	4.24	3.82 - 4.66	Acceptable	SM4500F- C 18th ED 1992	3/16/2012	-1.64	4.18	0.161	
1820	Nitrate + Nitrite as N	mg/L	4.23	4.29	3.65 - 4.93	Acceptable	EPA-126A 5.	2/27/2012	0.244	4.18	0.200	
1810	Nitrate as N	mg/L	4.23	4.29	3.86 - 4.72	Acceptable	EPA-126A 5	2/28/2012	0.297	4.18	0.180	
1125	Potassium	mg/L		20.7	17.6 - 23.8	Not Reported				20.7	1.48	
2000	Sulfate	mg/L		67.5	57.4 - 77.6	Not Reported				66.7	3.19	
1955	Total Dissolved Solids at 180°C	mg/L	513	513	410 - 616	Acceptable	SM2540C 18th ED 1992	2/16/2012	0.391	504	22.5	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

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EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID: WV00003

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
'S Inorganics (cat# 591)												
1505	Alkalinity as CaCO3	mg/L		114	103 - 125	Not Reported				112	4.43	
1575	Chloride	mg/L	82.7	81.7	69.4 - 94.0	Acceptable	EPA 300.0 2.1 1993	2/13/2012	1.04	80.2	2.44	
1610	Conductivity at 25°C	µmhos/cm		659	593 - 725	Not Reported				675	15.3	
1730	Fluoride	mg/L	4.16	4.24	3.82 - 4.66	Acceptable	EPA 300.0 2.1 1993	2/13/2012	-0.15	4.18	0.161	
1820	Nitrate + Nitrite as N	mg/L		4.29	3.65 - 4.93	Not Reported				4.18	0.200	
1810	Nitrate as N	mg/L	4.18	4.29	3.86 - 4.72	Acceptable	EPA 300.0 2.1 1993	2/13/2012	0.0190	4.18	0.180	
1125	Potassium	mg/L		20.7	17.6 - 23.8	Not Reported				20.7	1.48	
2000	Sulfate	mg/L	64.7	67.5	57.4 - 77.6	Acceptable	EPA 300.0 2.1 1993	2/13/2012	-0.625	66.7	3.19	
1955	Total Dissolved Solids at 180°C	mg/L		513	410 - 616	Not Reported				504	22.5	
'S pH (cat# 552)												
1900	pH	S.U.	8.00	8.03	7.83 - 8.23	Acceptable	EPA 150.1 1982	2/15/2012	-0.346	8.02	0.0506	
'S Solids Concentrate (cat# 5150)												
1960	Non-Filterable Residue (TSS)	mg/L	57.0	65.3	52.2 - 78.4	Acceptable	SM2540D 18th ED 1992	3/1/2012	-1.33	67.6	7.99	
1955	Total Dissolved Solids at 180°C	mg/L		466	373 - 559	Not Reported				472	14.3	
1950	Total Solids at 105°C	mg/L		547	438 - 656	Not Reported				545	14.7	

alytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

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EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID: WV00003

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
'S Metals (cat# 590)												
1000	Aluminum	µg/L		389	311 - 467	Not Reported				396	21.6	
1005	Antimony	µg/L		38.7	27.1 - 50.3	Not Reported				39.3	1.82	
1010	Arsenic	µg/L		28.0	19.6 - 36.4	Not Reported				28.5	1.88	
1015	Barium	µg/L		1540	1310 - 1770	Not Reported				1510	61.5	
1020	Beryllium	µg/L		16.0	13.6 - 18.4	Not Reported				15.9	0.593	
1025	Boron	µg/L		974	828 - 1120	Not Reported				976	62.2	
1030	Cadmium	µg/L		13.6	10.9 - 16.3	Not Reported				13.4	0.475	
1040	Chromium	µg/L		188	160 - 216	Not Reported				188	6.39	
1055	Copper	µg/L		1540	1390 - 1690	Not Reported				1520	52.8	
1070	Iron	µg/L	740	755	642 - 868	Acceptable	SM3111B 18th ED 1992	3/1/2012	-0.738	760	27.5	
1075	Lead	µg/L		32.4	22.7 - 42.1	Not Reported				32.6	1.82	
1090	Manganese	µg/L	490	515	438 - 592	Acceptable	SM3111B 18th ED 1992	3/1/2012	-2.4	527	15.3	
1100	Molybdenum	µg/L		20.7	17.6 - 23.8	Not Reported				20.6	1.04	
1105	Nickel	µg/L		264	224 - 304	Not Reported				262	10.0	
1140	Selenium	µg/L		75.2	60.2 - 90.2	Not Reported				75.2	4.10	
1150	Silver	µg/L		58.3	40.8 - 75.8	Not Reported				58.0	2.83	
1165	Thallium	µg/L		8.72	6.10 - 11.3	Not Reported				8.69	0.384	
1185	Vanadium	µg/L		467	397 - 537	Not Reported				466	18.0	
1190	Zinc	µg/L		793	674 - 912	Not Reported				800	31.8	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

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Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID: WV00003

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
'S Metals (cat# 590)												
1000	Aluminum	µg/L	396	389	311 - 467	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.00215	396	21.6	
1005	Antimony	µg/L	39.7	38.7	27.1 - 50.3	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.201	39.3	1.82	
1010	Arsenic	µg/L	29.8	28.0	19.6 - 36.4	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.674	28.5	1.88	
1015	Barium	µg/L	6010	1540	1310 - 1770	Not Acceptable	EPA 200.8 5.4 1994	2/21/2012	73.1	1510	61.5	
1020	Beryllium	µg/L	15.8	16.0	13.6 - 18.4	Acceptable	EPA 200.8 5.4 1994	2/21/2012	-0.173	15.9	0.593	
1025	Boron	µg/L		974	828 - 1120	Not Reported				976	62.2	
1030	Cadmium	µg/L	13.3	13.6	10.9 - 16.3	Acceptable	EPA 200.8 5.4 1994	2/21/2012	-0.155	13.4	0.475	
1040	Chromium	µg/L	199	188	160 - 216	Acceptable	EPA 200.8 5.4 1994	2/21/2012	1.75	188	6.39	
1055	Copper	µg/L	1590	1540	1390 - 1690	Acceptable	EPA 200.8 5.4 1994	2/21/2012	1.28	1520	52.8	
1070	Iron	µg/L		755	642 - 868	Not Reported				760	27.5	
1075	Lead	µg/L	34.1	32.4	22.7 - 42.1	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.834	32.6	1.82	
1090	Manganese	µg/L		515	438 - 592	Not Reported				527	15.3	
1100	Molybdenum	µg/L		20.7	17.6 - 23.8	Not Reported				20.6	1.04	
1105	Nickel	µg/L	275	264	224 - 304	Acceptable	EPA 200.8 5.4 1994	2/21/2012	1.25	262	10.0	
1140	Selenium	µg/L	73.4	75.2	60.2 - 90.2	Acceptable	EPA 200.8 5.4 1994	2/21/2012	-0.445	75.2	4.10	
1150	Silver	µg/L	60.1	58.3	40.8 - 75.8	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.721	58.0	2.83	
1165	Thallium	µg/L	9.01	8.72	6.10 - 11.3	Acceptable	EPA 200.8 5.4 1994	2/21/2012	0.842	8.69	0.384	
1185	Vanadium	µg/L		467	397 - 537	Not Reported				466	18.0	
1190	Zinc	µg/L	767	793	674 - 912	Acceptable	EPA 200.8 5.4 1994	2/21/2012	-1.04	800	31.8	

- corrected typo - accepted.

WS-187 2009 TNI Evaluation Final Complete Report

A Waters Company

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EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID: WV00003

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
'S Mercury (cat# 551)												
1095	Mercury	µg/L	6.86	7.60	5.32 - 9.88	Acceptable	EPA 200.8 5.4 1994	2/27/2012	-1.38	7.59	0.531	
'S Mercury (cat# 551)												
1095	Mercury	µg/L	7.26	7.60	5.32 - 9.88	Acceptable	EPA 245.1 3 1994	2/24/2012	-0.628	7.59	0.531	
'S Nitrite (cat# 594)												
1840	Nitrite as N	mg/L	1.71	1.73	1.47 - 1.99	Acceptable	2-013-1-H	2/23/2012	-0.138	1.72	0.0815	
'S Nitrite (cat# 594)												
1840	Nitrite as N	mg/L	1.70	1.73	1.47 - 1.99	Acceptable	EPA 300.0 2.1 1993	2/23/2012	-0.26	1.72	0.0815	
'S o-Phosphate Nutrients (cat# 558)												
1870	ortho-Phosphate as P	mg/L	2.11	1.98	1.68 - 2.28	Acceptable	EPA 300.0 2.1 1993	2/20/2012	1.53	1.98	0.0823	
'S Cyanide (cat# 556)												
1645	Cyanide, total	mg/L	0.134	0.147	0.110 - 0.184	Acceptable	SM4500CN F 18th ED 1992	2/28/2012	-0.95	0.148	0.0152	
'S Organic Carbon (cat# 557)												
1710	Dissolved Organic Carbon (DOC)	mg/L	5.21	6.26	5.55 - 6.89	Not Acceptable	EPA 415.3 1 2003	2/24/2012	-1.48	6.38	0.790	
2040	Total Organic Carbon (TOC)	mg/L		6.26	5.01 - 7.51	Not Reported				6.34	0.383	
'S Turbidity (cat# 592)												
2055	Turbidity	NTU	6.70	7.29	6.21 - 8.13	Acceptable	EPA 180.1 2 1993	2/16/2012	-1.24	7.15	0.362	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0520

WS-187 Laboratory Exception Report

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EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12
Agency ID:

There are no values reported with < where the assigned value was greater than 0.

2009 TNI Not Acceptable Evaluations

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WS Metals (cat# 590)							
1015	Barium	µg/L	6010	1540	1310 - 1770	Not Acceptable	EPA 200.8 5.4 1994
WS Organic Carbon (cat# 557)							
1710	Dissolved Organic Carbon (DOC)	mg/L	5.21	6.26	5.55 - 6.89	Not Acceptable	EPA 415.3 1 2003

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West Virginia Department of Health and Human Resources
Bureau for Public Health
Office of Laboratory Services
Environmental Chemistry Section

Standard Operating Procedure

Mercury Cold Vapor Atomic Absorption Standard Operating Procedures Using EPA Method 245.1

Prepared by: _____ **Date:** 10-10-06
Patrick Marchio, Chemist I

Reviewed by: _____ **Date:** 10-4-06
Larry Duffield, Program Manager

Approved by: _____ **Date:** 10-10-06
Dr. Andrea Labik, Laboratory Director

Periodic Review:

Signature	Title	Date
	Program Manager I	12-19-06 (revised)
	Program Manager I	4-3-08 (revised 5.4.4)

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Table of Contents

Section page

1. Summary of Method.....3
2. Interferences.....3
3. Equipment, Supplies, and Reagents.....3
4. Sample Handling and Preparation.....5
5. Quality Controls and Standards..... 6
6. Procedure and Data Analysis.....10
7. Maintenance.....12
8. Safety Precautions.....13
9. *References*.....13

Appendix page

A. Quality Controls and Corrective Action Summary.....14
B. EPA Alternative Test Procedure letter.....16
C. Software Deviations from Method Quality Controls and Sample Labels.....17

Freedom_0006095_0523

Mercury Cold Vapor Atomic Absorption Standard Operating Procedures Using EPA Method 245.1

1. Summary of Method

This method is used to measure total mercury (organic and inorganic) in drinking, surface, ground, sea, brackish waters and industrial and domestic wastewater. The range of this method used in this SOP is 0.2 to 10.0 µg/ L mercury (Hg). This is a reduced volume method that uses the same molar equivalents of reagents as listed in the EPA method. A 40 ml aliquot of a water sample is transferred to a 50 ml plastic digestion tube. The sample is then refluxed/ digested in a diluted potassium permanganate-potassium persulfate and acid solution and oxidized for 2 hours at 95 °C in a block digester. Mercury in the digested sample is then reduced with stannous chloride to elemental mercury. The mercury vapor from the sample is separated by a gas liquid separator and swept into an absorption cell mounted in the instrument with inert argon gas. The instrument makes absorbance readings based on a 253.65 nm wavelength using a CCD detector. This SOP contains alternate labels for quality controls that vary from the method labels. The purpose of these alternate labels is for automated calculations by the software.

2. Interferences

2.1. Interferences have been reported for waters containing sulfide, chloride, copper, and tellurium. Organic chemicals which have broad ultra-violet absorbance are confirmed interferences.

2.2. Volatile materials (e.g. chlorine) which absorb at 253.7 nm will cause a positive interference. Volatiles will come out of solution when samples are digested. Samples sit in the autosampler racks without caps allowing volatiles to escape into the air.

2.3. Ambient background mercury.

3. Equipment, Supplies, and Reagents

3.1. Equipment

- 3.1.1. Cetac M-6100 Cold Vapor Mercury Analyzer with autosampler
- 3.1.2. Digi-Prep block digester with temperature controller, see Appendix B for a letter of approval from the EPA.
- 3.1.3. Computer, software, and printer.
- 3.1.4. Calibrated thermometer checked annually against an NIST certified thermometer.
- 3.1.5. Analytical balance and weighing boats
- 3.1.6. Several bottle top reagent pipet dispensers.
- 3.1.7. Regulator and metering valve for Argon gas set to deliver gas at 40 psi with a flow of 125 ml/min.
- 3.1.8. Flowmeter capable of measuring 125 ml/min.

3.2. Supplies

- 3.2.1. Several 100, 250, 500 and 1000 ml class A volumetric flasks.

All glassware used in this procedure must be rinsed with 1+1 HNO_3 and Type I water.

3.2.2. 10, 50, 100, and 1000 µl adjustable pipettes with pre-cleaned tips.

3.2.3. 50,100 ml Class A graduated cylinders.

3.2.4. Several 50 ml Class A plastic digestion tubes with screw caps from SCP Scientific

3.2.5. Several 25 ml plastic autosampler tubes

3.2.6. 5 and 20 ml class A glass pipets.

3.2.7. pH paper

3.2.8. Peristaltic pump tubes

3.2.9. Compressed Ultra High Purity Argon gas

3.3. Reagents and Standards

3.3.1. ASTM Type I Reagent water with a resistivity ≥ 18.0 megohms/cm. If less, replace cartridges. The resistivity must be verified each day of use and recorded.

3.3.2. HNO_3 – Trace Metals grade

3.3.3. H_2SO_4 – Trace Metals grade

3.3.4. HCl - Trace metals grade

3.3.5. Potassium permanganate ($KMnO_4$) crystals- reagent grade

3.3.5.1 $KMnO_4$ solution – Dissolve 50 g. of $KMnO_4$ in 1 liter of reagent water in a class A volumetric flask.

3.3.5.2 This is also used to fill the mercury vapor scrubber on the back of the instrument.

3.3.6. Potassium persulfate ($K_2S_2O_8$) crystals- reagent grade

3.3.6.1 $K_2S_2O_8$ solution – Dissolve 50 g of $K_2S_2O_8$ in 1 liter of reagent water. in a class A volumetric flask.

3.3.7. Sodium chloride (NaCl) crystal – reagent grade

3.3.8. Hydroxlyamine hydrochloride ($NH_2OH{\cdot}HCl$) – reagent grade

3.3.8.1 Sodium chloride- Hydroxlyamine hydrochloride solution – Dissolve 120 g of each of the above reagents into 1 liter of reagent water in a class A volumetric flask.

3.3.9. Stannous chloride ($SnCl_2{\cdot}\ H_2O$) – reagent grade

3.3.9.1 10% $SnCl_2{\cdot}\ H_2O$ solution in 7% HCl: Add 25 g of $SnCl_2{\cdot}\ H_2O$ to a 250 ml volumetric flask half full of reagent water containing 17.5 ml concentrated HCl, dilute to volume and swirl to mix. To make 500 ml of this solution, dissolve 50g $SnCl_2{\cdot}\ H_2O$ into a 500 ml class A volumetric flash half full containing 35 ml HCL, then dilute to volume and swirl to mix. The use of HCl is allowed in Standard methods, 18th Edition - SM3112B, and was approved by EPA auditor Robin Costas.

3.3.10. Lab Reagent Blank (LRB) – prepare by dispensing reagent water into a 1 liter plastic jug, add 2 ml of HNO_3,shake to mix and let stand 16 hrs. before use. Document in logbook.

3.3.11. Mercury Stock Standards - Ultra Scientific 1000µg/ml Hg

3.3.11.1 Intermediate Standard 1.0 ppm – To a 100 ml class A volumetric flask half full, add 0.15 ml of conc. HNO_3. Add 100 µl of 1000µg/ml stock standard and dilute to volume. Invert several times to mix. Date and record in standards prep logbook. This standard should be prepared fresh each day of use.

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3.3.12. Laboratory Control Sample (LCS) stock also known as Quality Control Sample(QCS) – J.T. Baker 1000µg/ml Hg

3.3.12.1 LCS intermediate Solution 1.0 ppm- To a 100 ml class A volumetric flask half full, add 0.15 ml of conc. HNO_3. Add 100µL of 1000µg/ml stock LCS standard and dilute to volume. Invert several times to mix. This standard is used to prepare the quality control sample. Date and record in standards prep logbook. This standard should be prepared fresh each day of use.

3.3.13. Rinse water for the autosampler consists of a 1% solution of each HCl and HNO_3.

3.3.14. Rinse water for the GLS and pump tubes consist of a 5% solution of HCL.

3.3.15. 2-Propanol – used to clean the windows of the absorption cell.

4. Sample Handling and Preparation

4.1. Receiving- Samples received for metals analysis should be in an approved 1 liter or 1 quart pre-cleaned container, preferably plastic, and supplied by our lab. Samples not received in approved containers can be rejected. All samples are logged in and numbered. Samples should be received in lab within 2 weeks of collection, no ice required.

4.2. Preservation- Our lab does not recommend field preservation of metals samples due to hazards of acid and contamination. Unpreserved samples must be acidified upon receipt with 2 ml. concentrated nitric acid per liter volume. Mix thoroughly by capping and shaking. Note acidification with a blue "A" with date and time on cap. To ensure pH <2, check with pH test paper after sample has been allowed to set for 16 hours. If the pH is >2 add an additional 2 ml of HNO_3 and retest the pH after holding the sample for an additional 16 hrs. Document in Acidification/Digestion Logbook.

4.3. Holding Time- Following acidification, sample must be held for 16 hours before further processing. Preserved sample holding time is 28 days from time of collection.

4.4. Calibration standards and Sample preparation

4.4.1. Begin by pipetting the following amounts of the 1.0 ppm mercury standard (3.3.11.1) into 100 ml volumetric flasks half full of reagent water and containing 150 µl concentrated HNO_3

Standard	Volume of 1.0 ppm Hg standard used
Calibration Blank	0.0
0.2 ppb	20 µl
0.5 ppb	50 µl
1.0 ppb	100 µl
2.0 ppb	200 µl
5.0 ppb	500 µl
10.0 ppb	1000 µl

4.4.2. Dispense 40 ml of each standard using a 50 ml Class A graduated cylinder into a 50 ml plastic digestion tube.

4.4.3. Add 2.0 ml of H_2SO_4 and 1.0 ml HNO_3 to the standards in the plastic digestion tubes, and allow to cool.

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4.4.4. LCS preparation – prepare in the same manner as the above 5.0 ppb standard following steps 4.4.1 thru 4.4.3 using the LCS intermediate solution(3.3.12.1)

4.4.5. Prepare samples by dispensing a 40 ml aliquot of preserved sample into a plastic digestion tube using a class A graduated cylinder, then adding 2.0 ml of H_2SO_4 and 1.0 ml HNO_3, and allow to cool.

4.4.5. LFBs and Matrix spikes

4.4.5.1. Add 80 µL of 1.0 ppm Hg standard (3.3.11.1) to 40 ml aliquot of LRB labeled (LFB), and to all sample matrix spikes (MS). The resulting spike level will be 2.0 ppb

4.4.5.2. LFB at the MRL – Add 8 µL of 1.0 ppm Hg standard (3.3.11.1) to 40 ml aliquot of LRB labeled LFB-MRL.

4.4.6. To all the digestion tubes and standards add 6.0 ml of the $KMnO_4$ solution (3.3.5.1). Swirl to mix. Wait 15 minutes to make sure the permanganate color stays. If the permanganate color vanishes, add more permanganate and wait an additional 15 minutes before adding the $K_2S_2O_8$ solution (3.3.6.1).

4.4.7. To all the digestion tubes add 3.2 ml of the $K_2S_2O_8$ solution (3.3.6.1). Swirl to mix.

4.5. Digestion procedure

4.5.1. Digest only the **LRBs, LFBs, MS, MSDs, IDCs and all sample unknowns and spikes.**

4.5.2. Tightly screw caps onto plastic digestion tubes and place into the block digester.

4.5.3. Digest the above samples and QCs at 95°C. Begin by turning on the block digester at the control panel and set it to heat up to 95 °C, allow it to warm up and verify the temperature ± 2 °C using a calibrated thermometer placed in a tube with water at the same volume through a hole in a cap. Make adjustments to the temperature as necessary to achieve a digestion temperature of 95°C. Once to temperature, set the unit's timer for 2 hours. Samples will then digest for this amount of time and the unit will automatically shut off if programmed to.

4.6 After samples have digested and cooled, add 2.4 ml of Sodium chloride- Hydroxlyamine hydrochloride solution (3.3.8.1.)

4.7. Records- Records on each step of sample handling, i.e., receipt, acidification, digestion, completion, must be kept for each sample and entered in the sample prep logbook for this purpose.

5. Quality Controls and Standards

5.1. Initial Demonstration of Capability (IDC) – Before using this method to analyze drinking water, operator must determine or perform:

5.1.1. Linear Dynamic Range (LDR) - The upper limit of the LDR must be established for each analyte at each wavelength utilized. Determine this from readings from a minimum of six different concentration standards across the range, two of which are close to the upper limit of the LDR. LDRs must be documented and kept on file. The upper LDR limit should be an observed signal no more than 10% below the true value level extrapolated from the calibration standards. LDRs should be verified whenever there is a significant change in analytical performance.

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5.1.2. Instrument Detection Limit (IDL) –Take ten consecutive measurement readings of the calibration blank. Determine standard deviation between readings and multiply by 3. This is the IDL in ppm. Re-evaluate as deemed necessary. Record in QC book.

5.1.3. Method Detection Limit (MDL) – This is the minimum concentration with 99% confidence that it is greater than zero. Determine annually. Analyze seven replicates of Fortified Reagent Water (FRW) (See 5.4.5.) at 2-3 times the IDL concentration. FRW must be processed through entire analytical method including digestion. Determine standard deviation between readings of 7 replicates, multiply this by 3.14, this gives the MDL in ppm. Negative values of FRW readings are not valid.

5.1.4. Demonstration of Precision and Accuracy - It is determined by each analyst initially before analyzing compliance samples by analyzing four replicates of a known amount of analyte that has been put through the entire sample handling and preparation process. The accuracy limits is ±10% of true value. The precision acceptance limits for the IDC is < 10% RSD, if > 10% RSD then repeat analysis and/or re-make the IDC solution. The IDC solution is prepared from a second source standard, one not used to calibrate the instrument.

5.1.5. Analysis of an unknown with a recovery of +/- 10 % of true value.

5.2. Procedural Notes

5.2.1 Correlation Coefficient – This is calculated from the concentration of standards used in the calibration and their corresponding absorbance values. If it is greater than or equal to 0.995 continue analysis, if less than 0.995 stop and correct the problem and recalibrate. Record the correlation coefficient on raw data sheet.

5.2.2. Annual Proficiency Testing – Analyst must participate in annual Proficiency Testing study mandated by EPA. This involves analysis, using approved methods, of an unknown sample from a private vendor approved by EPA. Successful recovery of Hg is mandatory to retain certification. If it is not successfully recovered, method must be reviewed to determine cause and corrected. A Corrective Action Report must be forwarded to the Region 3 Certifying Authority. Participation in subsequent study will then be required with successful recovery expected for analyte in question.

5.2.3. Dilutions – If sample concentration is higher than highest calibration standard, sample must be diluted and reanalyzed until it is within calibration range. Prepare by taking an aliquot of digested sample and dilute with the calibration blank solution. Make note of dilution factor and apply when calculating concentration for reporting.

5.2.4. Reporting results – Results of analysis are to be reported as mg/l in three significant figures. If analyte quantity is less than the lowest calibration standard then report as "less than" (<) that standard concentration. Report date of analysis, analyst's initials, and method used.

5.2.5. Calculations – All calculations for analyte recovery and QC results whether performed automatically by computer or done manually must be accessible for

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review and kept on file for at least five years.

5.2.6. Data Reports – Raw data reports generated by instrument during analysis must be separated by year and kept on file for review for at least five years.

5.2.7. Quality Control Records – All results of quality control analysis must be recorded in a QC binder for that element. Results must be tabulated and LFBs graphed in appropriate charts to show relationship to previous data. If results appear consistently high or low, problem should be investigated, corrected, and documented.

5.2.8. The software of the computer system utilizes nomenclature that varies slightly from the EPA method quality control names. Using the software's designated names allows it to automatically calculate percent recoveries of standards and matrix spikes, and relative percent difference of sample duplicates. Otherwise hand calculation would be necessary. See Appendix C.

5.3. Blanks- Prepare as follows:

5.3.1. Lab Reagent Blank also known as a Preparation Blank (PBK)– This is reagent water that is treated exactly like a sample, including exposure to all glassware, plastic ware, equipment, digestion and reagents that are used on samples. To prepare, fill an approved metals sample container with Type I D.I. H_2O and add 2 ml. concentrated HNO_3 acid, mix thoroughly, and let stand 16 hr. and check the pH before further processing. Prepare one Preparation Blank for every 20 samples and put it through the entire digestion process.

5.3.2. Calibration Blank – This is Type I reagent water acidified such that the acid concentration and reagent matrix are identical to that of the calibration standards and samples. The software details two calibration blanks;

5.3.2.1. Initial calibration blanks (ICB) – those that immediately follow the initial calibration verification.

5.3.2.2. Continuing calibration blanks (CCB) – those that follow continuing calibration verifications.

5.4. Other quality controls

5.4.3. Lab Fortified Blanks (LFBs)

5.4.3.1. LFB - This is an aliquot of the Lab Reagent Blank that is spiked with a known quantity of analyte prior to digestion. The resulting spike concentration should be > 10X the MDL, but < the midpoint concentration of the calibration curve. Run 1 per 20 samples. Its purpose is to determine whether the method is in control and within accepted control limits of 85 – 115%. If recovery is outside of these limits, source of problem should be identified and resolved before continuing.

5.4.3.2. LFB-MRL - This is an aliquot of the Lab Reagent Blank that is spiked with a known quantity of analyte prior to digestion. The resulting spike concentration is at the reporting limit. Its purpose is to demonstrate that the instrument can detect the concentration of the lowest calibration standard when digested. Accepted control limits are 70-130 %. If recovery is outside of these limits, source of problem should be identified and resolved before

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continuing.

5.4.4. Sample Matrix Spike- (MSK) - This is an aliquot of unknown sample matrix to which a known quantity of analyte is added prior to digestion at the same concentration as the LFB. 10% of the samples are spiked or one per batch, whichever is greater. Add the same amount of working standard Hg solution as preparing the LFB to a duplicate sample aliquot in a plastic digestion tube. It is digested and analyzed exactly like a sample to determine whether the sample matrix and/or preparation method contributes bias to results. Recovery should be between 70-130%. If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery problem of the fortified sample is judged to be matrix related, not system related. Any matrix spike failures should be confirmed, if possible, by redigesting and reanalyzing to confirm the failure. If there is sufficient background analyte in the sample, the sample may also be diluted appropriately and reanalyzed to mitigate matrix interferences. If the failure is confirmed a second time on undiluted or diluted samples the result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix interferences. All matrix spikes are done in duplicate (MDUP).

5.4.5. Fortified Reagent Water (FRW) – this sample is essentially like the LFB but is made up with lower concentrations of analytes. It is used to determine the Method Detection Limit as discussed in section 5.1.3. After the analyst determines the Instrument Detection Limit (IDL), which is equal to three times the standard deviation of a series of ten replicate measurements of a calibration blank, an FRW sample is made up. To a one liter flask of Type I H_20, add levels of analyte to equal 2 – 3 times the IDL concentration. Add 2 ml conc. HNO_3, store in plastic sample bottle for at least 16 hr. before further processing.

5.4.6. Laboratory Duplicate (LDP) - This is a preparation duplicate of a sample that is taken through entire digestion process used determine if the digestion process affects precision. Comparison of results and action discussed can be found in appendix A.

5.4.7. Minimum Reporting Limit (MRL) - This is a LFB that matches the concentration of the lowest standard of the calibration curve. Accepted control limits are 70-130%.

5.4.8. Calibration Verifications 5.0 ppb (CVs) – The method calls this an Instrument Performance Check. This is an intermediate concentration calibration standard analyzed immediately after the initial calibration, after every 10 analyses, and at the end of the run that validates the calibration and stability of the instrument. The concentration is 50% of the highest calibration standard used.

5.4.8.1. Initial Calibration Verification (ICV) - immediately following the calibration- acceptance limits are +/- 5% recovery.

5.4.8.2. Continuing Calibration Verification (CCV) – subsequent calibration checks - acceptance limits are +/- 10% recovery.

5.4.9. Laboratory Control Sample (LCS) – This is a second source standard, one not used to calibrate the instrument, which is used to confirm the validity of the calibration and calibration standards. The acceptance limits are ± 10%.

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5.5. Records- The dates of preparation and initials of analyst must be recorded in the logbook for all blanks, standards, and quality controls discussed in section 5. Lot numbers must be documented for all solutions and reagents.

6. Procedure and Data Analysis

6.1 Initial Instrument Set-up

6.1.1. Secure the peristaltic pump tubes on to the pump as described in the instrument manual. Replace if tubes are worn or don't deliver an even flow.

6.1.2. Disconnect the black tubing going to the Nafion dryer from the gas liquid separator (GLS)

6.1.3. Open the regulator on the Argon cylinder and adjust the pressure to 60 psi, to aid in wetting of the GLS center post. Note this is optional and not necessary.

6.1.4. Power up the computer, printer, monitor, instrument, autosampler, and peristaltic pump.

6.1.5. Select the QuickTrace icon on the computer desktop to initialize the software, pumps, and mercury lamp

6.1.6. Allow at least 15 minutes for the mercury lamp to warm up.

6.1.7. Allow the center post of the GLS to become wet and reconnect the tubing going to the Nafion dryer after the GLS has drained.

6.1.8. Re-adjust the pressure regulator to 40 psi., check flowmeter and make adjustments with the metering valve to obtain a flow of 125 ml/min.

6.2 Instrument Sequence Set-up

6.2.1. Goto **File**, at the top of the page, scroll down and select, **New from**, and then select **Template**. The template worksheet is used to download instrument conditions and sequence information according to the concentration range desired for analysis.

6.2.2. From the list of template worksheets, select **Hg 0.2-10.0 ppb**.

6.2.3. Under template name enter the batch label to be used, for example, 091206a, would indicate month, date, year, and batch. 09/12/06 batch a. Another system of nomenclature is acceptable as long as it is explained and consistent. Integration with a LIMS system may require a different nomenclature than stated above. This is undetermined at this time and is pending.

6.2.4. To store data electronically, goto **window** at the top of the page and scroll down to **sequence parameters** and select **reports**. In report dialog box enter the file name and location where data is to be stored. For example C:\Hg_Data\09_06_Data\batch number (see 6.2.3. - 091206a)

6.2.5. Goto **window** at the top of the page and scroll down and select **sequence editor**.

6.2.6. Click the sequence box and enter the total number of samples to be run in the designated box, add more than is needed. They can be removed at a later time. Then select **Generate Sequence** at the bottom of the page. This will produce a sequence listing that begins with the predetermined calibration standards, initial quality control samples, and a sample listing that can be edited with the appropriate sample numbers, autosampler position and sample types. If more or less samples are needed goto **edit** at the top of the page and make the appropriate selection according to what is needed for the day of analysis.

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6.2.7. On the sequence table page enter the sample labels/ numbers according to the tube position on the autosampler. For example, tube position 1:5 indicates rack one, position five.

6.2.8. Enter sample type, this will tell the software whether the sample is a quality control or an unknown. Sample types in the software differ slightly from those listed in the method but their meaning is the same.

6.2.9. Once sequence information has been entered on the sequence page, right click the mouse, scroll down and select print sequence.

6.2.10. Set the instrument up so that it will go into stand-by mode after sequence is done by selecting window from the top tool bar. Scroll down and select sequence parameters. On the page that opens, check the box that says pump and select off. Select file from the top of the page and select save.

6.2.11. Load autosampler according to how it was entered into the sequence page.

6.2.12. Place the reagent sipper tube into the 10% $SnCl_2 \cdot H_2O$ solution.

6.2.13. Prior to calibrating the instrument, set the read times for the baseline drift and analyte peak by analyzing the 2 ppb Hg standard. To do this, select the Analyze single sample icon from the top tool bar. Enter the requested information and select OK. The analyzer will now read this preliminary sample. Observe and make note of the read time for the baseline and analyte peak. Goto Method Editor and make the necessary adjustments to these read times, then save this to the method. This will allow the instrument to compensate for daily variations of room temperature and pressure.

6.2.14. Select Go at the top of the page to start analysis.

6.2.15. Reports will be generated automatically at the end of the run.

6.2.16. Note: all the program conditions have been previously determined so that every time this worksheet (Hg 0.2- 10.0 ppb) is retrieved, the same instrument parameters will be used for analysis. Important - do not change the instrument parameters. If new parameters are desired then create a new method according to the analytical and detection limit needs.

6.3. Instrument shut down procedure

6.3.1. Remove the reagent sipper tube from the 10% $SnCl_2 \cdot H_2O$ solution, and place it into a container with 1%HNO_3/HCL. Allow this solution to flush out the pump tubes and GLS for several minutes. Upon completion remove the sipper tube and allow the pump tubes to completely empty.

6.3.2. Exit the QuickTrace software by selecting X at the top right hand corner of the page.

6.3.3. Release the tensioning clamps on the peristaltic pump, and remove the pump tubes from the tubing bridge.

6.3.4. Turn off the computer, and power supply transformers to the autosampler, analyzer, and peristaltic pump.

6.4 Methodology- Use only EPA approved methods for drinking water.

6.4.1 Approved Methods- EPA Method 245.1 "Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry. " Revision 3.0. May 1994

a. Modifications to method:

(1.) Use reagents as specified in this Standard Operating Procedure.

(2.) Use digestion procedure as described in this Standard Operating

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Procedure.

(3.) The Correlation Coefficient will automatically be calculated, if greater than or equal to 0.995 continue analysis, if less than 0.995 stop and correct problem and recalibrate.

(4.) Run matrix spikes (MSK) in duplicate (MDUP) on every 10 samples or 1 per batch. Recovery should be between 70-130%. If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery problem of the fortified sample is judged to be matrix related, not system related. The result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix effects. All samples are spiked duplicate. Calculate the RPD between duplicates. RPD must be <20%

(5.) LCS limits are +/-10% of true value. If outside limits, stop analysis and correct problem and document before repeating and continuing.

(6.) Run LRB. For each batch, or 1 per 20 samples, LRB should be less than MDL (See 5.3.1). LRB values that exceed the MDL indicate lab or reagent contamination. When LRB values are ≥ 10% of the analyte level determined for a sample or is 2.2 times the MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again after the source of contamination has been corrected and acceptable LRB values have been achieved.

(7.) Run a MRL for each batch, check against limits of +/- 30%. If above or below recovery limits, repeat analysis. If 2nd analysis is still outside limits, suspect poor precision, or analyte loss or contamination during preparation, consider raising lower limit of calibration curve, or investigate and correct.

(8.) Run both types of LFBs once per batch, or 1 per 20 samples. Calculate as percent recovery using the following equation:

$$R = [(LFB)/S] \times 100$$

Where: R= percent recovery

LFB= lab fortified blank, or LFB-MRL

S= concentrated equivalent of analyte added to fortify LRB solution.

The recovery limits are as follows:

LFB - control limits of 85-115%. If outside of limits, investigate and correct problem.

LFB-MRL - control limits of 70-130%. If outside of limits, investigate and correct problem.

7. Maintenance

7.1. Cleaning absorption cell windows- quartz windows need to be cleaned only when the Nafion dryer has been flooded and should be cleaned with 2-propanol as described in the operator's manual. Follow the manual for more specific directions.

7.2. Maintenance Log- Instrument Log is to be kept up to date. Record in detail any work done. Also record in detail any problems that occur during usage.

7.3. Service Contract- If service contract is maintained as recommended by EPA, keep on file for reference to determine coverage, etc.

7.4. **Important** - Thoroughly rinse analyzer's components of $SnCl_2$ by placing the sipper tube

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into a solution of 5% HCl and allowing the system to flush for 5- 10 minutes. Follow up with a DI water rinse.

7.5. Replace Nafion dryer and pump tubing as needed

7.6. Replace mercury lamp as needed.

7.7. Refresh the $KMnO_4$ in the scrubber when its color changes from purple to brown indicating the permanganate has oxidized.

7.8. Consult the instrument operator's manual for more detailed maintenance information.

8. Safety Precautions:

8.1. The toxicity and carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be minimized.

8.2. Mercury compounds are highly toxic if swallowed, inhaled or absorbed through the skin

8.3. Wear protective clothing, eye protection, and gloves when handling acids, standards, reagents, and samples.

8.4. Store Acid in the Acid cabinet.

8.5. Report all accidents and spills to the lab supervisor, use spill clean up kits located in metals prep room.

8.6. Clean up broken glass immediately and discard in proper container.

8.7. Store expired standards and reagents safely until a contractor can pick them up for disposal.

8.8. The compressed Argon gas cylinder must be strapped and immobile using the strap clamp attached to the desk.

9. References:

9.1. EPA Methods for the Determination of Metals in Environmental Samples, Supplement 1, EPA-600/R-94-111, May 1994.

9.2 EPA Manual for the Certification of Laboratories Analyzing Drinking Water, fifth edition, EPA 815-R-05-004, January 2005.

9.3 Standard Methods, 18th Edition, Method SM3112B, 1992

9.4 40 CFR Part 136 Appendix B

9.5 Cetac QuickTrace M-6100 Mercury Analyzer Operator Manual, Version 1.0.1

9.6 Cetac QuickTrace Mercury Analyzer Software Manual

Appendix A

Quality Control Limits And Corrective Action Summary For EPA 245.1

Calibration Verifications 5.0 PPB

LIMITS: Initial (ICV) ± 5.0 %

Continuing (CCV) ± 10.0 %

Corrective Action: Repeat: Upon second failure, cease analysis, recalibrate, repeat CCV or ICV Standard; reanalyze all samples back to last acceptable CCV.

Calibration Blanks (ICB & CCB) LIMITS: <MDL

Corrective Action: Repeat. Upon second failure, cease analysis, recalibrate, repeat CCV Standard and CCB, reanalyze all samples back to last acceptable CCV/CCB

Laboratory Control Sample (LCS) LIMITS: 90– 110%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause and rectify before continuing analysis.

Preparation Blank (PBK) LIMITS: <MDL, if samples contain Hg, the PBK values must be < 10% of sample analyte value, or < 2.2 times the MDL

Corrective Action: Repeat. Upon second failure, cease analysis, determine source of contamination and eliminate. If found necessary, re-digest sample batch before continuing.

Laboratory Fortified Blanks (LFBs)

LFB – LIMITS: 85-115%

LFB-MRL – LIMIST: 70-130%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause of analyte loss or source of contamination and rectify. If found necessary, re-digest sample batch before continuing.

Minimum Reporting Limit (MRL) LIMITS: 70– 130%

Corrective Action: Repeat. Upon second failure, cease analysis, determine cause and rectify before continuing. If MRL fails often, consider raising concentration level of the low standard of the curve and the MRL.

Laboratory Duplicate (DUP) LIMITS: ≤ 20%RPD

Corrective Action: Review sample preparation procedures, correct any observed problems and repeat sample and lab duplicate preparation and analysis

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<u>Sample Matrix Spike (MSK and MDUP)</u> LIMITS: 70–130% Recovery, 20% RPDs for spike duplicates

If the recovery is outside the limits and the laboratory performance is shown to be in control the recovery problem of the fortified sample is judged to be matrix related, not system related. Any matrix spike failures should be confirmed, if possible, by redigesting and reanalyzing to confirm the failure. If there is sufficient background analyte in the sample, the sample may also be diluted appropriately and reanalyzed to mitigate matrix interferences. If the failure is confirmed a second time on undiluted or diluted samples the result for the mercury sample must be labeled to inform the data user that the results are suspect due to matrix interferences.

Document all corrective actions in logbook.

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Appendix B

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAY - 8 2001.

OFFICE OF WATER

John Stone
Vice President
Environmental Express, Ltd
490 Wando Park Blvd.
Mt. Pleasant, SC 29464

Dear Mr. Stone:

This letter responds to your letter regarding the use of the Environmental Express HotBlock™ digestion system with EPA methods currently approved or soon to be proposed for the determination of mercury. Specifically your letter referenced EPA Methods 245.1, 245.2, 245.7 (to be proposed), 7470, 7471, and 1631. As stated in an earlier letter, EPA does not approve or endorse specific instrumentation However, provided that all procedures in the approved methods are followed, and all QA/QC criteria are met, the HotBlock™ is acceptable for use as a heating source in methods approved or proposed by EPA's Office of Water for use in National Pollutant Discharge Elimination System (NPDES) or National Primary Drinking Water Regulations (NPDWR) compliance monitoring. These methods include but are not limited to EPA Methods 245.1, 245.2, 245.7 and 1631.

For written clarification regarding the use of the Environmental Express HotBlock™ with EPA Methods 7470 and 7471, or other methods contained EPA's Office of Solid Waste methods manual, known as Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846), you will need to contact EPA's Office of Solid Waste. Written inquiries regarding SW-846 methods may be submitted to the following address: OSW Methods Team, U.S. Environmental Protection Agency Office of Solid Waste (5307W), Ariel Rios Building, 1200 Pennsylvania Ave. NW, Washington, DC 20460. Fax: 703-308-0511.

Alternatively, you may submit an inquiry through the Methods Information Communication Exchange (MICE) Service. The service provides timely answers to method-related questions and takes comments on technical issues regarding the EPA Office of Solid Waste methods. The MICE Service can be reached by telephone (703-676-4690), by fax (703-903-1373), or by e-mail: mice@epmx.saic.com.

If I can be of additional assistance on this and other matters, please write or call me at (202) 260-1639 at your convenience.

Sincerely,

Maria Gomez-Taylor

Maria Gomez-Taylor, Ph.D.
Analytical Method Staff
Engineering and Analysis Division (4304)

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Appendix C
Software Variations from Method Quality Controls and Sample Labels

Note: The purpose of these alternate labels is for automated calculations by the software.

Method Label	Software Label
Instrument Performance Check (IPC)	Initial Calibration Verification (ICV) Continuing Calibration Check(CCV)
Calibration Blank	Initial Calibration Blank (ICB) Continuing Calibration Blank (CCB)
Laboratory Reagent Blank (LRB)	Preparation Blank (PBK)
Quality Control Sample (QCS)	Laboratory Control Sample (LCS)
Laboratory Duplicate (LDP)	Duplicate (DUP)
Lab Fortified Sample Matrix (LFM)	Matrix Spike (MSK)
LFM Duplicate	Matrix Spike Duplicate (MDUP)

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West Virginia Department of Health and Human Resources
Bureau for Public Health
Office Laboratory Services
Environmental Chemistry Section

Standard Operating Procedure

Copper, Iron, Magnesium, Manganese, Sodium and Zinc
By
Direct Air-Acetylene Flame Atomic Absorption Spectrometry
Following
Standard Methods 18th Edition 3111 B

Prepared by: _____ Date: 1/11/07
Patrick Marchio, Chemist I

Reviewed by: _____ Date: 1-11-07
Larry A. Duffield, Program Manager

Approved by: _____ Date: 1-15-07
Dr. Andrea M. Labik, Laboratory Director

Periodic Review:

Signature	Title	Date

Project # Name:	SM3111B-2006
Revision #:	1
Date:	Oct 26,2006
Page:	1 of 20

Table of Contents

Section		Page
1.	Introduction	3
2.	Sample Requirements	3
3.	Reagents and Supplies	3
4.	Quality Control	9
5.	Procedure	13
6.	Data Analysis and Calculation	17
7.	Safety Precautions	17
8.	Procedure Notes	18q
9.	Reference	18

Appendix		Page
A -	Quality Control Limits and Corrective Action Summary	19

Metals in Drinking Water Measured in mg/L

Standard Methods 18th Edition 3111 B Direct Air Acetylene Fame Atomic Absorption Spectrometry

1. Introduction

A sample is aspirated into a flame and atomized. The light from a source lamp composed of the analyte being determined is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. One advantage of this method is it's relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range.

2. Sample Requirements

2.1. Sample Collection

A majority of the samples received in the laboratory are collected in pre-cleaned, 1-liter plastic bottles by sanitarians or district engineers. Samples not received in approved containers can be rejected. When a sample kit is sent to an individual the appropriate sampling instructions and container(s) are included.

2.2. Sample Preservation

The laboratory does not recommend field preservation of metals samples due to hazards of handling and shipment of acids. Unpreserved samples must be acidified upon receipt with 2 ml of concentrated nitric acid (HNO_3) per liter of sample to make the sample pH<2. Mix thoroughly by capping and shaking. Note acidification with the letter "A" and the date and time on cap of sample bottle. To ensure a pH<2, check with pH test paper after the sample(s) has been allowed to sit for 16 hours. If the pH is >2, add an additional 2 ml of HNO_3 and retest the pH after 16 hours. Continue until a pH of <2 is obtained. Record in the metals acidification/ digestion logbook along with date and time acidified. The method requires that the final acid concentration of samples and standards be at 5.2% HNO_3 in water. The addition of acid during the preservation step is accounted for while preparing samples for digestion.

2.3. Sample Storage

Store the samples on the cart in the metals laboratory prior to analysis. Following acidification, all samples must be held for 16 hours before further processing. Samples must be analyzed within 6 months of sample collection when preserved with HNO_3 to a pH of < 2.

2.4. Sample Rejection – Any regulatory compliance monitoring sample may be rejected for any of the specific reasons listed below that are not covered in the Environmental Chemistry Quality Assurance Manual.

2.4.1 Sample(s) received > 14 days from time of collection.

2.4.2 Sample(s) was collected in a bottle not provided/ approved by the laboratory.

2.4.3 Sample volume was less than required.

3. Reagents and Supplies

3.1 Reagents

3.1.1. Reagent water - resistivity ≥ 18.0 MΩ/cm – (ASTM Type I). Document water quality each day of use on the clipboard next to the purification system.

3.1.2. Nitric acid – use only trace metal grade.

3.1.3. Acetylene gas (Atomic Absorption Grade) with regulator
3.1.4. Lanthanum Nitrate [$La(NO_3)_3 \cdot 6H_2O$] – ACS grade or better

3.2. Supplies/ Equipment
3.2.1. Varian Spectra AA model 400 Plus with flame unit and consumables
3.2.2. Air Compressor
3.2.3. pH paper
3.2.4. Digestion blocks capable of maintaining a temperature @ 95°C ± 2°
3.2.5. 35ml Digestion tubes with caps for 3.2.4.
3.2.6. Digi-Prep Heated Block Digester capable of maintaining a temperature of 95° C ± 2°
3.2.7. 50ml Digestion tubes with caps for 3.2.6.
3.2.8. Glass block digester covers for both 3.2.4 and 3.2.6.
3.2.9. Several 100 and 1000ml Class A volumetric flasks
3.2.10. One 10ml Bottle-top dispenser
3.2.11. 1000, 100, 50 µL automated pipettes
3.2.12. 1-liter plastic bottles
3.2.13. Several thermometers capable of reading 95±1°C, checked annually against an NIST certified thermometer, and documented.
3.2.14. Balance capable of weighing to 0.01 g.
3.2.15. 50 ml Class A graduated cylinder

3.3. Solutions
3.3.1. Calibration Blank in 5.2% HNO_3 – Transfer approximately 500 ml of reagent water to a one liter class A flask and add 52 ml of HNO_3 and dilute to 1000 ml. Document in standards prep logbook. This is for determining copper, iron, manganese, sodium and zinc.
3.3.2. Magnesium Calibration Blank – prepare the same way as the above solution, except with the addition of 100 ml of $La(NO_3)_3 \cdot 6H_2O$ matrix modifier solution (3.3.5), and 27 ml HNO_3. The resulting acid concentration is 5.2%. See 3.3.8.1
3.3.3. Rinse Blank in 0.2% HNO_3 - Transfer approximately 1 liter for reagent water to a one liter sample bottle and 2 ml of HNO_3.
3.3.4. Laboratory Reagent Blank in 0.2% HNO_3 - Transfer approximately 1liter for reagent water to a new one liter sample bottle and 2ml of nitric acid. Allow this to sit for 16 hours before use.. Document in standards prep logbook.
3.3.5. Lanthanum Nitrate [$La(NO_3)_3 \cdot 6H_2O$] matrix modifier solution – Transfer approximately 250 ml of reagent water to a one liter class A volumetric flask and add 250 ml of HNO_3. Dissolve 151.5 g of $La(NO_3)_3 \cdot 6H_2O$ into the flask. Dilute to volume. This solution is used only for determining magnesium and is added to **all** standards, quality controls, blanks, and samples in a 1:10 ratio. **Because of the high acid content needed to dissolve the solid, the acid content for all standards, quality controls, blanks, and samples must be compensated to account for this additional acid. The final nitric acid concentration should be equal to 5.2%.**
3.3.6. Copper (Cu) stock standard 1000 mg/L – use Ultra Scientific Plasma Grade Standard or other of similar quality – see manufacture for expiration date. Put the certificate of analysis in the appropriate binder and date when received. Label standard bottle when received and opened.

3.3.6.1. 10 mg/L Cu intermediate standard – To a 100 ml flask add 50 ml of reagent water and 5.2 ml HNO_3. Transfer 1 ml of the Cu stock standard and dilute to 100 ml – expires in six months. Date and document in standards prep logbook.

3.3.6.2. Cu calibration standard 0.025 – 1.000 mg/L. Date and document in standards prep logbook. Date container used and these expire in 6 months.

Calibration Standards	Intermediate Solution (10 mg/L Cu)	Stock Solution (1000 mg/LCu)	Nitric Acid	Final Volume
0.025 mg/L Cu	250µl	-----	5.2ml	100ml
0.050 mg/L Cu	500µl	-----	5.2ml	100ml
0.100 mg/L Cu	1000µl	-----	5.2ml	100ml
0.500 mg/L Cu	-----	50µl	5.2ml	100ml
1.000 mg/L Cu	-----	100µl	5.2ml	100ml

3.3.7. Iron (Fe) stock standard 1000 mg/L – use Ultra Scientific Plasma Grade Standard or other of similar quality – see manufacturer for expiration date.

3.3.7.1. 10 mg/L Fe intermediate standard – To a 100 ml flask add 50 ml of reagent water and 5.2 ml HNO_3. Transfer 1ml of the Fe stock standard and dilute to 100 ml – expires in six months. . Document in standards prep logbook.

3.3.7.2. Fe calibration standards 0.05 – 1.00 mg/L. Document in standards prep logbook.

Calibration Standards	Intermediate Solution (10mg/L Fe)	Stock Solution (1000mg/L Fe)	Nitric Acid	Final Volume
Blank	-----	-----	5.2ml	100ml
0.05 mg/L Fe	500µl	-----	5.2ml	100ml
0.10 mg/L Fe	1000µl	-----	5.2ml	100ml
0.25 mg/L Fe	2500µl	-----	5.2ml	100ml
0.50 mg/L Fe	-----	50µl	5.2ml	100ml
0.60 mg/L Fe	-----	60µl	5.2ml	100ml
1.00 mg/L Fe	-----	100µ	5.2ml	100ml

3.3.8. Magnesium (Mg) stock standard 1000 mg/L - use Ultra Scientific Plasma Grade Standard or other of similar quality – see manufacturer for expiration date. Put the certificate of analysis in the appropriate binder and date when received. Label standard bottle when received and opened. Lot numbers are documented in standard preparation logbook.

3.3.8.1. Mg calibration standards 0.50 – 5.00 mg/L. Date and document in standards prep logbook. Date container used and these expire in 6 months.

Calibration Standards	Lanthanum Nitrate matrix modifier	Stock Solution (1000mg/LMg)	Nitric Acid	Final Volume
Blank	100 ml	-----	27 ml	1000ml
0.50 mg/L Mg	10 ml	50 µl	2.7ml	100ml
1.00 mg/L Mg	10 ml	100 µl	2.7ml	100ml
2.50 mg/L Mg	10 ml	250 µl	2.7ml	100ml
5.00 mg/L Mg	10 ml	500 µl	2.7ml	10 ml

3.3.9. Manganese (Mn) stock standard 1000 mg/L – use Ultra Scientific Plasma Grade Standard or other of similar quality –see manufacturer for expiration date

3.3.9.1. 10 mg/L Mn intermediate standard – To a 100 ml flask add 50 ml of reagent water and 5.2ml HNO_3. Transfer 1 ml of the Mn stock standard and dilute to 100 ml – expires in six months. Document in standards prep logbook.

3.3.9.2. Mn calibration standards 0.02 – 0.50 mg/L Mn. Document in standards prep logbook.

Calibration Standards	Intermediate Solution (10mg/L Mn)	Stock Solution (1000mg/LMn)	Nitric Acid	Final Volume
Blank	-----	-----	5.2ml	100ml
0.02 mg/L Mn	200µl	-----	5.2ml	100ml
0.05 mg/L Mn	500µl	-----	5.2ml	100ml
0.10 mg/L Mn	1000µl	-----	5.2ml	100ml
0.20 mg/L Mn	2000µl	-----	5.2ml	100ml
0.50 mg/L Mn	-----	50µl	5.2ml	100ml

3.3.10. Sodium (Na) stock standard1000 mg/L – use Ultra Scientific Plasma Grade Standard or other of similar quality – see manufacturer for expiration date.

3.3.10.1. Na calibration standards 2.00 – 20.00 mg/L Na. Document in standards prep logbook.

Calibration Standards	Stock Solution (1000mg/L Na)	Nitric Acid	Final Volume
Blank	-----	5.2ml	100ml
2.00 mg/L Na	200µl	5.2ml	100ml
5.00 mg/L Na	500µl	5.2ml	100ml
10.00 mg/L Na	1000µl	5.2ml	100ml
15.00 mg/L Na	1500µl	5.2ml	100ml
20.00 mg/L Na	2000µl	5.2ml	100ml

3.3.11. Zinc (Zn) stock standard1000 mg/L – use Ultra Scientific Plasma Grade Standard or other of similar quality – see manufacturer for expiration date.

3.3.11.1. 2.00 mg/L Zn intermediate standard – To a 100 ml flask add 50 ml of reagent water and 5.2 ml HNO_3. Transfer 100 µl of the Zn stock standard and dilute to 100 ml – expires in six months. Document in standards prep logbook.

3.3.12. Laboratory Fortified Blank- Minimum Reporting Limit Spiking Solution (LFB-MRL)

3.3.12.1. LFB – MRL Spiking Solution #1- expires in one year. Document in standards prep logbook. Prepare as shown below:

Analyte	Stock Solution (1000mg/L)	Final LFB-MRL Spiking Solution Concentration	Nitric Acid	Final Volume
Iron (Fe)	5.0 ml	5.0 mg/L	2.0 ml	1000 ml
Manganese (Mn)	2.0 ml	2.0 mg/L		
Zinc (Zn)	2.0 ml	2.0 mg/L		
Copper (Cu)	2.5 ml	2.5 mg/L		
The LFB-MRL spiking solution for Sodium is the Stock Standard (3.3.9)				

350 µl of the above solution into 35 ml of lab reagent blank will result in a spike concentration of 0.05 mg/L for Fe, 0.02 mg/L for Mn and Zn, 0.025 mg/L for Cu. 70 µl of the sodium stock standard will result in a spike concentration of 2.0 mg/L.

3.3.12.2. LFB – MRL Spiking Solution #2 – for magnesium only- expires in one year. Document in standards prep logbook. Prepare as shown below:

Analyte	Stock Solution (1000mg/L)	Final LFB-MRL Spiking Solution Concentration	Nitric Acid	Final Volume
Mg	5.0 ml	50.0 mg/L	0.20 ml	100 ml

500 µl of the above solution into 50 ml of lab reagent blank will result in a spike concentration of 0.50 mg/L of Mg.

Note: Solutions 3.3.11.1 and 3.3.12.1 can be prepared with the other metal analytes found in method SM3113B with the same matrix.

3.3.13. Quality Control Sample (QCS) – These are prepared from second source standards of a different brand that are not used to prepare calibration standards or the solutions listed above and expire in one year. Use plasma grade standards or other of similar quality. Document in standards prep logbook. Prepare as shown below:

3.3.13.1. Quality Control Sample (QCS) for the following metals:

Analyte	Stock Solution (1000mg/L)	Final QCS solution concentration	Nitric Acid	Final Volume
Fe	250 µl	0.25 mg/L	52 ml	1000 ml
Mn	250 µl	0.25 mg/L		
Na	10.0 ml	10.0 mg/L		
Zn	250 µl	0.25 mg/L		
Cu	200 µl	0.20 mg/L		

3.3.11.2. Zn calibration standard 0.02 – 1.00 mg/L Zn. Document in standards prep logbook.

Calibration Standards	Intermediate Solution (2 mg/L Zn)	Stock Solution (1000mg/L Zn)	Nitric Acid	Final Volume
Blank	-----	-----	5.2ml	100ml
0.02 mg/L Zn	1000µl	-----	5.2ml	100ml
0.05 mg/L Zn	2500µl	-----	5.2ml	100ml
0.10 mg/L Zn	5000µl	-----	5.2ml	100ml
0.25 mg/L Zn	-----	25µl	5.2ml	100ml
0.50 mg/L Zn	-----	50µl	5.2ml	100ml
1.00 mg/L Zn	-----	100µl	5.2ml	100ml

3.3.11. Laboratory Fortified Matrix Spiking Solutions (LFM Spiking Solution) - expires in one year. Document in standards prep logbook. These solutions are used to prepare lab fortified blanks and sample matrix spikes. Prepare as shown below:

3.3.11.1 LFM Spiking Solution #1

Analyte	Stock Solution (1000mg/L)	Final LFM Spiking Solution Concentration	Nitric Acid	Final Volume
Iron (Fe)	25 ml	25 mg/L	2.0 ml	1000 ml
Manganese (Mn)	25 ml	25 mg/L		
Zinc (Zn)	25 ml	25 mg/L		
Copper (Cu)	8.0 ml	8.0 mg/L		
The LFM spiking solution for Sodium is the Stock Standard (3.3.9)				

350 µl of the above solution(s) into 35 ml of sample will result in a spike concentration of 0.25 mg/L for Fe,Mn,Zn, 0.080 mg/L for Cu and 10 mg/L for Na.

3.3.11.2. LFM Spiking Solution #2 – for Magnesium only- expires in one year. Document in standards prep logbook. Prepare as shown below:

Analyte	Stock Solution (1000mg/L)	Final LFM Spiking Solution Concentration	Nitric Acid	Final Volume
Mg	10 ml	100 mg/L Mg	0.20 ml	100 ml

500 µl of the above solution into 50 ml of sample will result in a spike concentration of 1.00 mg/L Mg.

3.3.13.2. Quality Control Sample (QCS) for Magnesium:

Analyte	Stock Solution (1000mg/L)	Final QCS solution concentration	Lanthanum Nitrate matrix modifier	Nitric Acid	Final Volume
Mg	250 µl	2.50 mg/L	10.0 ml	2.7 ml	100 ml

3.3.14. Certificates of Analysis of all stock standards solutions, and reagents are logged into a binder kept in the lab with the date they were received. Record the date received and opened on the bottle labels.

4. Quality Control (See Appendix A for a summary of QC limits and corrective actions)
   4.1. Initial Demonstration of Capability
      4.1.1. The Initial Demonstration of Capability (IDC) is completed successfully before an analyst analyzes any compliance samples. The IDC is used in demonstrating that the analyst has the ability to achieve the precision and accuracy required by the method and to meet the lab's data quality objectives and program requirements.
      4.1.2. The IDC solution is a sample matrix containing a known concentration of the method analyte in water, which is used to fortify reagent water.
      4.1.3. The spiking solution stock must be obtained from a source not used to prepare the laboratory calibration standards. The analyst can use the stock quality control sample (QCS) standards to prepare the IDC solution.
      4.1.4. At least four aliquots of the IDC solution must be carried through the entire sample preparation procedure and must be digested.
      4.1.5 Recovery must fall within 90 - 110%. If recovery of analyte exceeds control limits, corrective action must be taken and documented. Analysis of all four aliquots must be repeated until all four pass successfully.
      4.1.6. The Relative Standard Deviation (RSD) must be < 10%. If the RSD exceeds the control limits corrective action must be taken and documented. Repeat the analytical procedure until successful.
      4.1.7. The stock solution source and lot number used in determining the IDC must be recorded on the instrument print out along with the concentration and units.
      4.1.8. The IDC data must be submitted on a summary sheet and approved by the supervisor and kept on file for review.
      4.1.9. The analyst must successfully quantify the analysis of an unknown before analyzing drinking water compliance samples. The unknown will be a Proficiency Test from an EPA approved PT provider. The true value and acceptance limits of which are unknown to the analyst.
   4.2. Instrument Detection Limit
      4.2.1. Instrument detection limit (IDL) is the concentration equivalent that produces a signal equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank at the same wavelength. (3x SD_{10})
   4.3. Method Detection Limit
      4.3.1. Method detection limit (MDL) is the minimum concentration of an analyte that can be identified with 99% confidence that the analyte concentration is greater then zero.
      4.3.2. The MDL is determined by analyzing seven replicates of fortified reagent water (FRW), that has concentration at least two or three times the estimated instrument detection limit(IDL).

The FRW should be analyzed over a period of three non-consecutive days. Each successive day all seven FRW's must be analyzed.

4.3.3. It is recommended that more than one FRW concentration be analyzed.

4.3.4. If the relative standard deviation of the seven replicates is <10% the FRW concentration may have been inappropriately high for the determination of the MDL.

4.3.5. Negative results for MDL studies are invalid.

4.3.6. MDL = 3.14 x (standard deviation of the seven replicates). The final MDL is determined by the mean over the three day period.

4.3.7. Determined annually or after major instrument maintenance is performed.

4.3.8. The MDL data must be submitted on summary sheets and approved by the supervisor and kept on file.

4.4. Quality Control Sample

4.4.1. A quality control sample (QCS) is a sample solution containing a method analyte or a mixture of the method analytes in a reagent water matrix containing 5.2% HNO_3

4.4.2. Should be obtained from a source external to the laboratory, or a source different from those used for calibration standards.

4.4.3. Analyzed at least once per quarter in which that analyte that was tested or to verify new calibration standards, or daily to meet data quality objectives.

4.4.4. Recovery must fall within 90 - 110%. If recovery of analyte exceeds control limits, repeat analysis. If the quality control limits are exceeded on the second analysis the analyst should cease analysis, determine the cause, and rectify and if need be make new calibration standards and/ or QCS. Recalibrate and test again.

4.5. Laboratory Reagent Blank

4.5.1. Laboratory Reagent Blank (LRB) is reagent grade water treated exactly as a sample to assess contamination from the environment. LRB values that exceed the MDL indicate that laboratory or reagent contamination should be suspected.

4.5.2. The LRB must be carried through the entire sample preparation procedure and must be digested

4.5.3. LRB must be analyzed with each batch of 20 or fewer samples of the same matrix.

4.5.4. Corrective actions - If LRB values are > MDL, repeat analysis. If the LRB fails on second analysis, the sample batch must be re-digested. If LRB fails again, a fresh LRB sample must be prepared, samples re-digested and analyzed again after the source of contamination has been corrected. Document all corrective actions taken in corrective actions logbook.

4.5.5. The LRB is made by filling a new sample bottle with reagent water and adding 2 ml of nitric acid. This solution must stand for 16 hours before any aliquots can be taken.

4.6. Laboratory Fortified Blanks

4.6.1. Laboratory Fortified Blank (LFB) is a known quantity of the method analyte added to reagent water in the laboratory. This is used to verify the complete laboratory analysis procedure from sample preparation to analysis.

4.6.1.1 The LFB concentration should be the same as the concentration used in spiking the laboratory fortified sample matrix.

4.6.1.2 The LFB at the reporting limit (LFB-MRL) is at the concentration of the lowest calibration standard.

4.6.2. The LFBs must be carried through the entire sample preparation procedure and must be digested.

4.6.3. LFBs must be analyzed with each batch of 20 or fewer samples of the same matrix.

4.6.4. LFB and LFB-MRL Preparation:

4.6.4.1. The LFB for Fe, Mn, Na, Cu, and Zn is prepared by transferring 35 ml of the LRB solution to a 35 ml digestion tube and adding 350 µl of the LFM Spiking Solution and 1750 µl of HNO_3.

4.6.4.2. The LFB for Mg is prepared by transferring 50 ml of the LRB solution to a 50 ml digestion tube and adding 500 µl of the LFM Spiking Solution, 5.0 ml of the lanthanum nitrate matrix modifier, and 1250 µl of HNO_3.

4.6.4.3. The LFB-MRL for Fe, Mn, Na, Cu, and Zn is prepared by transferring 35 ml of the LRB solution to a 35 ml digestion tube and adding 350µl of the LFM-MRL Spiking Solution and 1750µl of HNO_3.

4.6.4.4. The LFB-MRL for Mg is prepared by transferring 50 ml of the LRB solution to a 50 ml digestion tube and adding 500µl of the LFM-MRL Spiking Solution, 5.0 ml of the lanthanum nitrate matrix modifier, and 1250 µl of HNO_3.

4.6.5. Control limits:

4.6.5.1. LFB recovery limits are 85 to 115%. If the recovery of the analyte exceeds control limits, repeat the analysis. Upon second failure the analyst should cease analysis and identify the source of contamination or loss and resolve before continuing analysis. Corrective action must be taken and documented. Calibration standards must be reanalyzed if results are exceeded on second analysis. Re-digestion of samples may be necessary.

4.6.5.2. LFB-MRL recovery limits are 70 to 130%. If the recovery of the analyte exceeds control limits, repeat the analysis. Upon second failure the analyst should cease analysis and identify the source of contamination or loss and resolve before continuing analysis. Corrective action must be taken and documented. Calibration standards must be reanalyzed if results are exceeded on second analysis. Re-digestion of samples may be necessary

4.7. Minimum Reporting Limit

4.7.1. The Minimum Reporting Limit (MRL) is reagent water spiked with a concentration of analyte that is equal to the lowest calibration standard used in the daily calibration of the instrument. This is used to verify the laboratory's reporting limit.

4.7.2. The MRL must be analyzed with each analysis.

4.7.3. The MRL is the low calibration standard. It is not digested.

4.7.4. Control limits for the MRL recovery are 80 to 120%. If the recovery of the analyte exceeds control limits corrective action must be taken and documented. Calibration standards must be reanalyzed if results are exceeded on second analysis. The analyst may consider raising the MRL level or perform extensive instrument maintenance if the control limits are exceeded often.

4.8. Instrument Performance Check Solution

4.8.1. Instrument Performance Check Solution (IPC) is a known quantity of the method analyte added to reagent water in the laboratory. This solution is used in assessing the performance of the instrument.

4.8.2. IPC must be analyzed immediately following the calibration curve, after every tenth sample and at the end of the run.

4.8.3. The IPC is prepared in the same manner as the calibration standards and is one chosen from the midpoint of the calibration range. The IPC for Fe, Mn, and Zn is at a concentration of 0.25 mg/L. The IPC for Na is at a concentration of 10 mg/L. The IPC for Mg is at a concentration of 2.5 mg/L. The calibration standard at these concentrations may be analyzed as the IPC.

4.8.4. Control limits for the IPC recovery are 90 to 110%. If the recovery of the analyte exceeds control limits corrective action must be taken and documented. Calibration standards and samples must be reanalyzed if results are exceeded on second analysis up to the last acceptable IPC standard.

4.9. Quality Control Blank

4.9.1. A Quality Control Blank (QC BLANK) is used to assure that contamination of the analytical system will be detected, if present.

4.9.2. Must be analyzed immediately following every IPC, after every tenth sample and at the end of the run.

4.9.3. The QC BLANK is prepared in the same manner as the calibration blank. The calibration blank may be analyzed as the QC BLANK.

4.9.4. Control limits for the QC BLANK is <IDL but > negative IDL. If the limit is exceeded corrective action must be taken and documented. Upon second failure stop analysis, recalibrate and reanalyze all samples up to the last acceptable IPC standard.

4.10. Laboratory Fortified Sample Matrix

4.10.1. Laboratory fortified sample matrix (LFM) is a known quantity of the method analyte added to an environmental sample in the laboratory.

4.10.2. A minimum of 10% of the routine samples must be spiked with the appropriate analyte solution of known concentration.

4.10.3. The LFM must be carried through the entire sample preparation procedure and must be digested

4.10.4. The known quantity of the method analyte used in the LFM should be a concentration that is equal to the LFB. Spike concentrations are 0.25 mg/L for Fe, Mn, Zn, 10 mg/L for Na, 0.20 mg/L for Cu, and 1.0mg/L for Mg.

4.10.5. LFM Preparation:

4.10.5.1. The LFM for Fe, Mn, Na, and Cu is prepared by transferring 35 ml of the sample to a 35 ml digestion tube and adding 350 µl of the LFM Spiking Solution and 1750 µl of HNO_3.

4.10.5.2. The LFM for Mg is prepared by transferring 50 ml of sample to a 50 ml digestion tube and adding 500 µl of the LFM Spiking Solution, 5.0 ml of the lanthanum nitrate matrix modifier, and 1250 µl of HNO_3.

4.10.6. Control limit for the LFM recovery are 70 to 130%. If recovery of analyte exceeds control limit corrective action must be taken and documented.

4.10.6.1. A matrix effect has taken place if control limits have been exceeded the second time and the QCS and LFB are within control limits. Results for the sample must be flagged to inform the customer the results are suspect due to a matrix effect. See Reference 9.2, Section 7.2.6.

4.10.6.2. If the spike concentration is <25% of the background analyte the percent recovery does not need to be calculated.

4.11. Digested Duplicate

4.11.1 The Digested Duplicate (DDP) is run to determine if the digestion process influences method precision.

4.11.2. The DDP must be carried through entire sample preparation procedure and one must be ` digested and analyzed with every 20 samples or one per batch.

4.11.3. Relative percent difference (RPD) must fall within < 20%. If the relative percent difference exceeds control limits this may indicate that the sample was not kept homogenous during dispensing prior to digestion and/or contamination occurred during the digestion process and corrective actions must be initiated and documented.

4.12. Laboratory Duplicate

4.12.1. The Laboratory Duplicate (LDP) is run to determine instrument precision. It is a consecutive analysis of the same aliquot of sample.

4.12.2. The LDP is analyzed after every 10 samples or at least 1 per batch.

4.12.3. Relative percent difference must fall within < 10%. If the relative percent difference exceeds control limits corrective action must be taken. Repeat analysis until the relative percent difference is <10%.

4.12.4. Analyte recoveries <MRL are not valid for precision assessment. If this is the case then a LFM duplicate should be ran for precision.

5. Procedure

5.1. Glassware Preparation

5.1.1. All glassware used in this procedure must be rinsed with a 50% HNO_3 solution.

5.1.2. There is no clean up of the sample containers and digestion tubes; these are disposable.

5.2. Calibration standards

5.2.1. The calibration standards are prepared according to section 3.3 and must be analyzed in order from low to high concentration, starting with the blank.

5.3. Sample Preparation

5.3.1. Invert sample several times to insure proper mixing.

5.3.2. To ensure the sample was preserved at a pH<2, check with pH test paper and record in the metals acidification / digestion logbook along with date and time acidified. (See section 2.2)

5.3.2.1 If sample was not maintained at the correct pH, add 2 ml of HNO_3 to 1 liter of sample and hold for an additional 16 hours and repeat this section again.

5.3.3.After completing the preservation check of the sample(s), prepare in the following manner for Fe, Mn, Na, and Cu:

	LRB Solution	Sample Volume	LFM Spiking Solution	LFM-MRL Spiking Solution	Stock Sodium Standard 1000ug/ml	Nitric Acid	Digested
LRB	35 ml	---	---	---	---	1750 µl	Yes
LFB	35 ml	---	350 µl	----	350 µl	1750 µl	Yes
LFB-MRL	35 ml	---	---	350 µl	70 µl	1750 µl	Yes
Sample	---	35 ml	---	---	---	1750 µl	Yes
DDP	---	35 ml	---	---	---	1750 µl	Yes
LFM	---	35 ml	350 µl	---	350 µl	1750 µl	Yes

5.3.4. After completing the preservation check of the sample(s), prepare in the following manner for Mg:

	LRB Solution	Sample Volume	Lanthanum Nitrate matrix modifier	LFM Spiking Solution	LFM-MRL Spiking Solution	Nitric Acid	Digested
LRB	50 ml	---	5.0 ml	---	---	1250 µl	Yes
LFB	50 ml	---	5.0 ml	500 µl	----	1250 µl	Yes
LFB-MRL	50 ml	---	5.0 ml	---	500 µl	1250 µl	Yes
Sample	---	50 ml	5.0 ml	---	---	1250 µl	Yes
DDP	---	50 ml	5.0 ml	---	---	1250 µl	Yes
LFM	---	50 ml	5.0 ml	500 µl	---	1250 µl	Yes

5.4. Digestion Procedure

5.4.1. Total Recoverable

5.4.1.1. Place the 35 ml samples in the block digesters located in the large fume hood and the 50 ml samples for Mg in the large block digester in the small fume hood. Each digestion block must have a temperature control sample.

5.4.1.2. The temperature control sample is prepared by placing a thermometer in a digestion tube and filled with reagent water at the same level as the samples.

5.4.1.3. Cover the digestion tubes with the glass cover plate and evaporate the sample down to about 20% of volume (1-1¼inch from bottom) at 95°C. Do not let the sample evaporate to dryness during digestion.

5.4.1.4. The sample should be clear. If not, continue heating and add HNO3 as necessary.

5.4.1.5. Let sample cool to room temperature and dilute to mark with reagent water, cap and mix thoroughly.

5.5. Instrument Setup

5.5.1. With the instrument turned off remove the graphite furnace automated sampler and furnace if installed and place them on the holder located on the end of the instrument. Next, remove the mirror used in checking the position of the sample tip in the furnace.

5.5.2. Take the spray chamber / nebulizer assembly out of the storage and attach it inside the instrument compartment.

5.5.3. Attach the drain hoses to the spray chamber / nebulizer assembly and make sure the water level in the waste container is below each hose.

5.5.4. With a squirt bottle containing reagent water, dispense into the burner hole until water drains from lower drain hose.

5.5.5. Attach the burner assembly in line with the lamp beam, except when determining Na and Mg which require the burner to be turned 90°, due to the intensity of their ions.

5.5.6. Next attach the sample tray to the outside bottom of the instrument compartment. The analyst will be protected from the open flame by attaching the shield to the front of the instrument compartment.

5.5.7. The chimney must be in position on top of the instrument compartment and the fume hood can be turned on.

5.5.8. Plug in the compressor and it will begin pressurizing the holding tank. When the compressor turns off, open acetylene supply valve located above the compressor.

5.5.9. The acetylene must be turned on outside in the storage area. The exiting acetyelene pressure at the tank must be set to 70 psi by turning the large knob located on the regulator. Do not use the tank if the pressure is below 100 psi. The acetylene line entering the laboratory behind the Varian Instrument must be open.

5.5.10. To check and see if the correct lamp is installed and in the correct position open the lamp turret cover and rotate the turret to check. If the lamp is not installed follow the step bellow. Lamp turret positions for each analyte can be found on the *instrument parameters* page of the software.

5.5.9.1. Turn the turret until the lamp slot needed is located in the front.

5.5.9.2. Hold the installed lamp at its base and press the white retaining button to release.

5.5.9.3. Now install the required analyte lamp by lining up the pins and index slot with the empty turret slot while still pressing the white retaining button. Release the white retaining button once the lamp is seated.

5.5.11. Turn the computer, monitor, printer, and spectrometer on in this order so each peace of equipment is able to communicate in the proper sequence.

5.5.12. If the instrument is in *furnace mode* press the **F10** key to bring up the *index* page and press **F2** to switch the instrument to *flame mode*.

5.5.13. Press the **F10** key again to display the *index* page and select *Sequence Selection* by entering **10** and press **ENTER**. From this menu press **F1** to clear the current program and enter the number of the desired program and press **F6** to initiate. The spectrometer will automatically rotate the proper lamp into position and setup the lamp according to the pre-program configuration file.

5.5.14. The lamp needs to be optimized now; this can be done by going back to the *index* page **F10** and selecting *Optimization* and press **ENTER**. By turning the two black knobs located on the back of the lamp turret the x-axis and y-axis of the lamp can be adjusted for maximum energy. If a D2 lamp is being used for background correction the x-axis and y-axis can be adjusted by the two black knobs located inside the front portion of the turret compartment. D2 background correction is not used for Na but is used for the other metals listed in this SOP.

5.5.15. Raise the burner by turning the height adjustment knob located underneath the spray chamber / nebulizer assembly until the lamp intensity begins to drop. Now lower the burner height so the burner is just beneath the light beam. (back to original lamp intensity).

5.5.16. To ignite the flame press the **Ignite Button** located on the right front panel of the instrument. If the flame does not ignite on the first try wait for the chamber to air out and try again. After the flame is ignited the software will adjust it to the program settings. After flame is adjusted place the sample introduction capillary in the rinse blank and wait 30 minutes for the instrument to equilibrate.

5.5.17. Return back to the index page **F10** and select the *Optimization* page and press **ENTER**. After the instrument is equilibrated the lamp should be realigned again for maximum energy. While aspirating a high standard, optimize the horizontal burner adjustment.

5.5.18. Wavelengths used are: Cu- 324.8 nm, Fe- 248.3 nm, Mg- 285.2, Mn- 279.5 nm, Na- 589.6 nm, and for Zn-213.9 nm.

5.6. Software Setup

5.6.1. The settings for each program are stored in the software, however if a program should become corrupted the settings from the last run are printed.

5.6.2. From the index page select *Report Format* by entering **13** and press **ENTER**. On this page

enter the name of the analyst and date of analysis.

5.6.3. Select *Sample Label* page from the *index* page by selecting 14 and press ENTER. The samples and needed quality controls are entered according to the run sequence. After all information is entered the sample schedule can be printed by pressing PRINT SCREEN key.

5.7. Analysis

5.7.1. To begin analysis press the *Start* key F11 and the printer will print the heading and program settings. The screen will prompt the analyst to press the *Read* key F9 for a blank. This will print out the heading for the instrument readout as well as print the results of the rinse blank.

5.7.2. Press the *Stop* key F12 and pause the instrument so it can be returned to manual mode. Return to the *index* page and select *Sequence Selection* and re-enter the desired program again. This will return the instrument to manual mode.

5.7.3. Return back to the index page F10 and select the *Optimization* page and press ENTER, now record the photomultiplier voltage.

5.7.4. Return to the index page and select *Calibration* by entering 15 and press ENTER. While aspirating the calibration blank, press SHIFT F10 to zero the instrument.

5.7.5. In the upper left corner of the computer screen the software will display the standard, sample or quality control needed based upon the *Sample Label* page and program settings. To make the first reading for the calibration curve press the *Read* key F9 while aspirating the calibration blank. The software is setup to take three replicates and print.

5.7.6. After printing the results transfer the sample introduction capillary into the rinse blank and the instrument is ready for the next sample. Proceed through the calibration standards starting with the lowest calibration standard. Then proceed with the analysis of the rest of the sequence. The run should appear in this order:

1) Calibration blank
2) Calibration standards
3) Instrument Performance Check (IPC)
4) Quality Control Blank (QC BLANK)
5) Quality Control Sample (QCS)
6) Laboratory Reagent Blank (LRB)
7) Reporting Limit Verification (RLV)
8) Laboratory Fortified Blank at the Minimum Reporting Limit (LFB-MRL)
9) Laboratory Fortified Blank (LFB)
10) Sample
11) Sample - Laboratory Duplicate (LDP)
12) Sample - Digested Duplicate (DDP)
13) Sample - Laboratory Fortified Sample Matrix 1 (LFM1)
14) LFM2 – need if sample value is < MRL
15) Instrument Performance Check (IPC)
16) Quality Control Blank (QC BLANK)

5.7.6. After analyses is complete, remove the sample introduction capillary from the rinse blank and press the **RED BUTTON** located on the front right panel of the instrument to shutdown the flame.

5.7.7. Next, close the valve to the acetylene line and the regulator attached to the acetylene cylinder. Unplug the compressor. Turn off the fume hood, instrument, printer, monitor and computer in this order.

5.7.8. If any maintenance was performed this must be recorded in the Instrument Logbook.

6. Data Analysis and Calculation
   6.1. Calculations
      6.1.1. Using a calculator based linear regression curve fitting technique plot the concentration values of the calibration standards against the instrument response (absorbance).
      6.1.2. The correlation coefficient must be > 0.995. If this condition is not met then corrective action must be taken and documented and re-calibrate the instrument. Record the correlation coefficient on the data sheet.
      6.1.3. Sample concentration is computed by comparing sample response with the standard curve. The instrument automatically performs this calculation and is printed on the raw data sheet.
      6.1.4. All manual calculations must be recorded on the raw data sheet.
   6.2. Data Analysis
      6.2.1. The report must be signed by the analyst.
      6.2.2. Report only those values that fall between the lowest and highest calibration standards.
      6.2.3. If the results are below the lowest calibration standard then the results must be reported as < (value of lowest calibration standard) mg/L. Example <0.05 mg/L Fe. If the results are > the highest calibration standard, dilute until sample readings are within the calibration range and apply this dilution factor when calculating data to achieve the final sample concentration.
      6.2.4. Report results as mg/L using three significant figures.
      6.2.5. When a sample is analyzed in duplicate report the first results only. This is done because each analysis is in triplicate. LDP and DDP are analyzed for instrument and method precision.
      6.2.6. All quality control results must be recorded in the Quality Control binder. The laboratory fortified blank must be graphed. If any of the quality control results appear consistently low or high the problem should be investigated and corrected.

7. Safety Precautions
   7.1. Protective Equipment
      7.1.1. Safety precautions must be taken when handling acids, reagents and samples. Protective clothing including lab coats, safety glasses and gloves should be worn.
      7.1.2. A spill kit is located in room #1 under the dry chemical storage cabinet and room #2 by the sink.
      7.1.3. Perform all digestion in a fume hood that provides an average face velocity of > 100 linear feet per minute.
      7.1.4. The gas cylinders must be located in a protected area outside the building in the cylinder storage shed which must be locked at all times.
   7.2. Chemicals
      7.2.1. Acetylene is explosive when exposed to an oxidizer and caution must be taken when handling cylinders. The cylinders must be secured in a manner to prevent tipping.
      7.2.2. If solutions come into contact with your eyes, flush with cold water continuously for 15 minutes. If solutions come in contact with your skin, wash thoroughly with soap and water. Get medical attention immediately if ingested.
      7.2.3. All spills should be reported to the supervisor as soon as possible.
      7.2.4. Material Safety Data Sheets (MSDS) are inside the blue MSDS binder located in room#1 by the reagent cabinets.

7.2.5. All reagents used in this laboratory are located in rooms #1 and #2.

7.3. Waste Management

7.3.1. Chemicals that have exceeded the shelf life or expiration date must be disposed of by a waste disposal company

8. Procedure Notes

8.1. Chemical interference occurs when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the current flame temperature. Interferences when determining Mg is reduced with the use of the lanthanum nitrate matrix modifier solution.

8.2. Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors.

8.3. The D2 lamp will have lower intensities than the line source hollow-cathode lamp. To obtain a valid D2 background correction, match the intensities of the D2 and hollow-cathode lamp. However, this may result in lowering the intensity and may have the disadvantage of raising the detection limit and possibly causing nonlinearity of the calibration curve.

9. References

9.1. "Manual for the Certification of Laboratories Analyzing Drinking Water" 5th Edition, January 2005, EPA 815-R-05-004

9.2. "Technical Notes on Drinking Water Methods", EPA-600/R-94-173, October 1994

9.3. CFR 40 Part 136, Appendix B

9.4. "Standard Methods for the Examination of Water and Wastewater" 18th Edition, 1992

Appendix A
Quality Control Limits and Corrective Action Summary
Record all corrective actions in logbook

Quality Control Parameter	Cu, Fe, Mg, Mn, Na, Zn Limits
Quality Control Sample (QCS) Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause. If found necessary prepare new calibration standards and new QCS.	100 ± 10% Rec.
Instrument Performance Check (IPC) Corrective Action: Repeat until second failure. Upon second failure stop analysis and recalibrate instrument and reanalyze all sample back to last acceptable IPC.	100 ± 10% Rec.
Quality Control Blank (QC BLANK) Corrective Action: Repeat until second failure. Upon second failure stop analysis and recalibrate instrument and reanalyze all samples back to last acceptable IPC.	-IDL < QC BLANK < IDL
Laboratory Reagent Blank (LRB) Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine source of contamination and eliminate. Redigest any affected samples.	< MDL
Laboratory Fortified Blank (LFB) Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause of analyte loss or source of contamination and eliminate. Redigest any affected samples.	100 ± 15% Rec.
LFB-MRL Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause of analyte loss or source of contamination and eliminate	100± 30% Rec.
Minimum Reporting Limit (MRL) Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause. If the MRL fails often, consider raising the concentration.	100 ± 20% Rec.
Laboratory Duplicate (LDP) Corrective Action: Repeat . Upon second failure cease analysis and determine cause of lack of instrument precision	<10% RPD
Laboratory Fortified Sample Matrix (LFSM) Corrective Action: Repeat until second failure. Upon second failure stop analysis and determine cause. A matrix effect has taken place if control limit is exceeded the second time and the QCS and LFB are within control limits. The results must be flagged when reported.	100 ± 30% Rec.

Digested Duplicate (DDP)	<20% RPD
Corrective Action: Repeat. A second failure would indicate the sample was not kept homogenous during dispensing prior to digestion and/or contamination occurred during the digestion process. Investigate and rectify, and repeat entire sample preparation process and repeat analysis.	

MDL = Method Detection Limit IDL= Instrument Detection Limit REC = Analyte Recovery RPD = Relative Percent Difference

Note: All corrective actions taken for failed quality controls must be documented in logbook.

Pat MDLs

INITIAL DEMONSTRATION OF CAPABILITY
Method Detection Limit – Data Summary

Method	EPA 200.8 Revision 5.4	Analyte	Sb,As,Ba,Be,Cd,Cr,Cu,Pb,Ni,Se,Ag,Tl,Zn
SOP Number/Revision	ICPMS2008	Date Completed	5/21/10

Instrument Name and Model Number	Perkin Elmer Elan 9000
Instrument Software (version)	Elan 3.4
Reason for Study	Validation of new instrument
Source of Calibration Standard (Name/Lot #)	VHG (001-0069R)
Quality Control Sample (Name/Lot #)	Accustandard (B8105037-1A)
Date Fortified Reagent Water was Made	4/26/10
Date Sample and Quality Control was Digested	4/27/10
Concentration of Fortified Reagent Water	1.0 µg/L

Replicate	1	2	3	4	5	6	7	Standard Deviation	MDL
Analysis Date	See Attachment								
Results									

Method Detection Limit (MDL) = SD * T

Where,

T = Student's T value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [T = 3.14 for seven replicates].
SD = Standard deviation of the replicate analysis.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Pat Marlin
Analyst

Gregory W Young 11-24-10
HHR Program Manager – Environmental Chemistry

12-23-10
HHR Program Manager – Quality Control Coordinator

Revision 2.0

INITIAL DEMONSTRATION OF CAPABILITY
Precision and Accuracy - Data Summary

Analyst: Patrick Marchio

Concentration units: µg/L

Analyte (Mass)	Fortified Reagent Water		REPLICATES							Standard Deviation	Method Detection Limit
	True Value	Date Analyzed	1	2	3	4	5	6	7		
			5/12/2010	5/12/2010	5/12/2010	5/18/2010	5/18/2010	5/21/2010	5/21/2010		
Beryllium (9)	1.000		0.938	0.953	0.924	0.969	0.983	0.985	0.966	0.0227	0.0714
Chromium (52)	1.000		1.308	1.250	1.223	1.223	1.228	1.207	1.196	0.0369	0.1160
Cobalt (59)	1.000		1.006	1.009	0.990	1.022	1.037	1.022	1.020	0.0150	0.0471
Nickel (60)	1.000		1.176	0.973	1.076	1.069	1.014	1.131	1.134	0.0715	0.2244
Copper (63)	1.000		1.238	1.001	1.139	1.069	1.047	1.220	1.123	0.0879	0.2761
Zinc (66)	1.000		1.356	1.313	1.469	1.632	1.717	1.415	1.370	0.1516	0.4760
Arsenic (75)	1.000		0.764	0.870	0.888	0.996	0.772	0.938	0.902	0.0841	0.2641
Selenium (82)	1.000		0.747	0.840	0.824	0.908	0.774	0.733	0.810	0.0602	0.1890
Silver (107)	1.000		0.950	0.951	0.963	0.977	0.997	0.998	0.983	0.0201	0.0631
Cadmium (111)	1.000		0.986	0.954	0.949	0.919	0.922	0.941	0.957	0.0228	0.0716
Antimony (123)	1.000		1.041	1.020	0.996	0.934	0.894	1.136	1.058	0.0803	0.2520
Barium (137)	1.000		0.987	0.977	0.980	0.992	0.983	1.032	1.008	0.0196	0.0615
Thallium (205)	1.000		1.008	1.008	0.993	1.003	1.026	1.045	1.020	0.0172	0.0540
Lead (208)	1.000		0.997	0.987	0.989	1.027	1.037	1.054	1.026	0.0259	0.0814

125 Market Street
New Haven, CT 06513
USA

AccuStandard, Inc.

Tel (203)786-5290
Fax (203)786-5287
Website AccuStandard.com

CERTIFICATE OF ANALYSIS

Rec 10/13/09

AccuTrace™ Reference Standard

Item Number: ICP-MS-QC2-1

Mix Name: ICP-MS Quality Control Sample 2 **Lot Number:** B8105037-1A

Matrix: 5% HNO3 **Expiration Date:** Oct / 2011

Elements in µg/mL

		SRM#			SRM#			SRM#
Al	10	3101a	Fe	10	3126a	Tl	10	3158
Sb	10	3102a	Pb	10	3128	Th	10	3159
As	10	3103a	Mg	10	3131a	U	10	3164
Ba	10	3104a	Mn	10	3132	V	10	3165
Be	10	3105a	Mo	10	3134	Zn	10	3168a
Cd	10	3108	Ni	10	3136			
Ca	10	3109a	K	10	3141a			
Cr	10	3112a	Se	10	3149			
Co	10	3113	Ag	10	3151			
Cu	10	3114	Na	10	3152a			

The total maximum uncertainty on the certified value(s) is ±2%. See reverse side of certificate for details.

In order to verify the concentrations, the final solution was checked against material traceable to the listed NIST SRMs by plasma emission spectroscopy (ICP)

RESULTS: This solution standard was certified for accuracy of major elemental constituency via methodology traceable to primary or well characterized secondary standards. All trace level elements and impurities were determined via plasma emission spectroscopy on the concentrate.

This standard was prepared gravimetrically to contain the elemental concentrations shown above. Balances, used in the preparation, are calibrated regularly using NIST-traceable weights. All glassware used in preparation is Class A.

We use the highest purity raw materials available, including high purity acids, ASTM type I 18 megohm deionized water, and typically 99.999%+ starting materials to minimize impurity levels in the final solution.

All bottles are acid leached and then triple rinsed with deionized water prior to use.

Use good laboratory procedure when diluting this product. Shake bottle prior to use and do not pipette directly out of the bottle. Use only cleaned Class A volumetric glassware.

We certify the accuracy of this standard to be ± 0.5% of the stated value until the expiration date listed above, provided it is kept tightly capped and stored under normal laboratory conditions.

L. Snyder

Lydia Snyder
Inorganic QC Supervisor

AccuStandard is accredited to ISO/IEC 17025:2005 and certified to ISO 9001:2000

OR-ORG/INO-001
Rev. 9/08

SmartTune Wizard - Summary

Optimization Summary

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7. References

1. KINGSTON, H.M. & L.B. JASSIE, eds. 1988. Introduction to Microwave Sample Preparation: Theory and Practice. American Chemical Soc., Washington, D.C.

2. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1990. Microwave assisted acid digestion of aqueous samples and extracts. SW-846 Method 3015, Test Methods for Evaluating Solid Waste. U.S. Environmental Protection Agency, Washington, D.C.

3110 METALS BY ATOMIC ABSORPTION SPECTROMETRY

Because requirements for determining metals by atomic absorption spectrometry vary with metal and/or concentration to be determined, the method is presented as follows:

Section 3111, Metals by Flame Atomic Absorption Spectrometry, encompasses:

- Determination of antimony, bismuth, cadmium, calcium, cesium, chromium, cobalt, copper, gold, iridium, iron, lead, lithium, magnesium, manganese, nickel, palladium, platinum, potassium, rhodium, ruthenium, silver, sodium, strontium, thallium, tin, and zinc by direct aspiration into an air-acetylene flame (3111B),
- Determination of low concentrations of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc by chelation with ammonium pyrrolidine dithiocarbamate (APDC), extraction into methyl isobutyl ketone (MIBK), and aspiration into an air-acetylene flame (3111C),
- Determination of aluminum, barium, beryllium, calcium, molybdenum, osmium, rhenium, silicon, thorium, titanium, and vanadium by direct aspiration into a nitrous oxide-acetylene flame (3111D), and
- Determination of low concentrations of aluminum and beryllium by chelation with 8-hydroxyquinoline, extraction into MIBK, and aspiration into a nitrous oxide-acetylene flame (3111E).

Section 3112 covers determination of mercury by the cold vapor technique.

Section 3113 concerns determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin by electrothermal atomic absorption spectrometry.

Section 3114 covers determination of arsenic and selenium by conversion to their hydrides and aspiration into an argon-hydrogen or nitrogen-hydrogen flame.

3111 METALS BY FLAME ATOMIC ABSORPTION SPECTROMETRY*

3111 A. Introduction

1. Principle

In flame atomic absorption spectrometry, a sample is aspirated into a flame and atomized. A light beam is directed through the flame, into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own characteristic absorption wavelength, a source lamp composed of that element is used; this makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments also are equipped for operation in an emission mode.

2. Selection of Method

See Section 3110.

3. Interferences

a. Chemical interference: Many metals can be determined by direct aspiration of sample into an air-acetylene flame. The most troublesome type of interference is termed "chemical" and results from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution. For example, the interference of phosphate in the magnesium determination can be overcome by adding lanthanum. Similarly, introduction of calcium eliminates silica interference in the determination of manganese. However, silicon and metals such as aluminum, barium, beryllium, and vanadium require the higher-temperature, nitrous oxide-acetylene flame to dissociate their molecules. The nitrous oxide-acetylene flame also can be useful in minimizing certain types of chemical interferences encountered in the air-acetylene flame. For example, the interference caused by high concentrations of phosphate in the determination of calcium in the air-acetylene flame is reduced in the nitrous oxide-acetylene flame.

MIBK extractions with APDC (see 3111C) are particularly useful where a salt matrix interferes, for example, in seawater. This procedure also concentrates the sample so that the detection limits are extended.

Brines and seawater can be analyzed by direct aspiration but sample dilution is recommended. Aspiration of solutions containing high concentrations of dissolved solids often results in solids buildup on the burner head. This requires frequent shutdown of the flame and cleaning of the burner head. Preferably use background correction when analyzing waters that contain in excess of 1% solids, especially when the primary resonance

* Approved by Standard Methods Committee, 1993.

line of the element of interest is below 240 nm. Make more frequent recovery checks when analyzing brines and seawaters to insure accurate results in these concentrated and complex matrices.

Barium and other metals ionize in the flame, thereby reducing the ground state (potentially absorbing) population. The addition of an excess of a cation (sodium, potassium, or lithium) having a similar or lower ionization potential will overcome this problem. The wavelength of maximum absorption for arsenic is 193.7 nm and for selenium 196.0 nm—wavelengths at which the air-acetylene flame absorbs intensely. The sensitivity for arsenic and selenium can be improved by conversion to their gaseous hydrides and analyzing them in either a nitrogen-hydrogen or an argon-hydrogen flame with a quartz tube (see Section 3114).

b. Background correction: Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of three types of background correction: continuum-source, Zeeman, or Smith-Hieftje correction.

1) Continuum-source background correction—A continuum-source background corrector utilizes either a hydrogen-filled hollow cathode lamp with a metal cathode or a deuterium arc lamp. When both the line source hollow-cathode lamp and the continuum source are placed in the same optical path and are time-shared, the broadband background from the elemental signal is subtracted electronically, and the resultant signal will be background-compensated.

Both the hydrogen-filled hollow-cathode lamp and deuterium arc lamp have lower intensities than either the line source hollow-cathode lamp or electrodeless discharge lamps. To obtain a valid correction, match the intensities of the continuum source with the line source hollow-cathode or electrodeless discharge lamp. The matching may result in lowering the intensity of the line source or increasing the slit width; these measures have the disadvantage of raising the detection limit and possibly causing nonlinearity of the calibration curve. Background correction using a continuum source corrector is susceptible to interference from other absorbing lines in the spectral bandwidth. Miscorrection occurs from significant atomic absorption of the continuum source radiation by elements other than that being determined. When a line source hollow-cathode lamp is used without background correction, the presence of an absorbing line from another element in the spectral bandwidth will not cause an interference unless it overlaps the line of interest.

Continuum-source background correction will not remove direct absorption spectral overlap, where an element other than that being determined is capable of absorbing the line radiation of the element under study.

2) Zeeman background correction—This correction is based on the principle that a magnetic field splits the spectral line into two linearly polarized light beams parallel and perpendicular to the magnetic field. One is called the pi (π) component and the other the sigma (σ) component. These two light beams have exactly the same wavelength and differ only in the plane of polarization. The π line will be absorbed by both the atoms of the element of interest and by the background caused by broadband absorption and light scattering of the sample matrix. The σ line will be absorbed only by the background.

Zeeman background correction provides accurate background correction at much higher absorption levels than is possible with continuum source background correction systems. It also virtually eliminates the possibility of error from structured background. Because no additional light sources are required, the alignment and intensity limitations encountered using continuum sources are eliminated.

Disadvantages of the Zeeman method include reduced sensitivity for some elements, reduced linear range, and a "rollover" effect whereby the absorbance of some elements begins to decrease at high concentrations, resulting in a two-sided calibration curve.

3) Smith-Hieftje background correction—This correction is based on the principle that absorbance measured for a specific element is reduced as the current to the hollow cathode lamp is increased while absorption of nonspecific absorbing substances remains identical at all current levels. When this method is applied, the absorbance at a high-current mode is subtracted from the absorbance at a low-current mode. Under these conditions, any absorbance due to nonspecific background is subtracted out and corrected for.

Smith-Hieftje background correction provides a number of advantages over continuum-source correction. Accurate correction at higher absorbance levels is possible and error from structured background is virtually eliminated. In some cases, spectral interferences also can be eliminated. The usefulness of Smith-Hieftje background correction with electrodeless discharge lamps has not yet been established.

4. Sensitivity, Detection Limits, and Optimum Concentration Ranges

The sensitivity of flame atomic absorption spectrometry is defined as the metal concentration that produces an absorption of 1% (an absorbance of approximately 0.0044). The instrument detection limit is defined here as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection limits vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the detection limit and extends to the concentration at which the calibration curve starts to flatten. To achieve best results, use concentrations of samples and standards within the optimum concentration range of the spectrometer. See Table 3111:I for indication of concentration ranges measurable with conventional atomization. In many instances the concentration range shown in Table 3111:I may be extended downward either by scale expansion or by integrating the absorption signal over a long time. The range may be extended upward by dilution, using a less sensitive wavelength, rotating the burner head, or utilizing a microprocessor to linearize the calibration curve at high concentrations.

5. Preparation of Standards

Prepare standard solutions of known metal concentrations in water with a matrix similar to the sample. Use standards that bracket expected sample concentration and are within the method's working range. Very dilute standards should be prepared daily from stock solutions in concentrations greater than 500 mg/L. Stock standard solutions can be obtained from several commercial sources. They also can be prepared from National In-

TABLE 3111:I. ATOMIC ABSORPTION CONCENTRATION RANGES WITH DIRECT ASPIRATION ATOMIC ABSORPTION

Element	Wave-length *nm*	Flame Gases*	Instrument Detection Limit *mg/L*	Sensitivity *mg/L*	Optimum Concentration Range *mg/L*
Ag	328.1	A–Ac	0.01	0.06	0.1–4
Al	309.3	N–Ac	0.1	1	5–100
Au	242.8	A–Ac	0.01	0.25	0.5–20
Ba	553.6	N–Ac	0.03	0.4	1–20
Be	234.9	N–Ac	0.005	0.03	0.05–2
Bi	223.1	A–Ac	0.06	0.4	1–50
Ca	422.7	A–Ac	0.003	0.08	0.2–20
Cd	228.8	A–Ac	0.002	0.025	0.05–2
Co	240.7	A–Ac	0.03	0.2	0.5–10
Cr	357.9	A–Ac	0.02	0.1	0.2–10
Cs	852.1	A–Ac	0.02	0.3	0.5–15
Cu	324.7	A–Ac	0.01	0.1	0.2–10
Fe	248.3	A–Ac	0.02	0.12	0.3–10
Ir	264.0	A–Ac	0.6	8	—
K	766.5	A–Ac	0.005	0.04	0.1–2
Li	670.8	A–Ac	0.002	0.04	0.1–2
Mg	285.2	A–Ac	0.0005	0.007	0.02–2
Mn	279.5	A–Ac	0.01	0.05	0.1–10
Mo	313.3	N–Ac	0.1	0.5	1–20
Na	589.0	A–Ac	0.002	0.015	0.03–1
Ni	232.0	A–Ac	0.02	0.15	0.3–10
Os	290.9	N–Ac	0.08	1	—
Pb†	283.3	A–Ac	0.05	0.5	1–20
Pt	265.9	A–Ac	0.1	2	5–75
Rh	343.5	A–Ac	0.5	0.3	—
Ru	349.9	A–Ac	0.07	0.5	—
Sb	217.6	A–Ac	0.07	0.5	1–40
Si	251.6	N–Ac	0.3	2	5–150
Sn	224.6	A–Ac	0.8	4	10–200
Sr	460.7	A–Ac	0.03	0.15	0.3–5
Ti	365.3	N–Ac	0.3	2	5–100
V	318.4	N–Ac	0.2	1.5	2–100
Zn	213.9	A–Ac	0.005	0.02	0.05–2

* A–Ac = air-acetylene; N–Ac = nitrous oxide-acetylene.
† The more sensitive 217.0 nm wavelength is recommended for instruments with background correction capabilities.
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stitute of Standards and Technology (NIST) reference materials or by procedures outlined in the following sections.

For samples containing high and variable concentrations of matrix materials, make the major ions in the sample and the dilute standard similar. If the sample matrix is complex and components cannot be matched accurately with standards, use the method of standard additions, 3113B.4*d*2), to correct for matrix effects. If digestion is used, carry standards through the same digestion procedure used for samples.

6. Apparatus

a. Atomic absorption spectrometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a device for vaporizing the sample (usually a flame), a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment.

b. Burner: The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot; a three-slot Boling head, which may be preferred for direct aspiration with an air-acetylene flame; or a special head for use with nitrous oxide and acetylene.

c. Readout: Most instruments are equipped with either a digital or null meter readout mechanism. Most modern instruments are equipped with microprocessors or stand-alone control computers capable of integrating absorption signals over time and linearizing the calibration curve at high concentrations.

d. Lamps: Use either a hollow-cathode lamp or an electrodeless discharge lamp (EDL). Use one lamp for each element being measured. Multi-element hollow-cathode lamps generally pro-

TABLE 3111:II. INTERLABORATORY PRECISION AND BIAS DATA FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD %	Relative Error %	No. of Participants
Direct determination:					
Aluminum[1]	4.50	0.19	4.2	8.4	5
Barium[2]	1.00	0.089	8.9	2.7	11
Beryllium[1]	0.46	0.0213	4.6	23.0	11
Cadmium[3]	0.05	0.0108	21.6	8.2	26
Cadmium[1]	1.60	0.11	6.9	5.1	16
Calcium[1]	5.00	0.21	4.2	0.4	8
Chromium[1]	3.00	0.301	10.0	3.7	9
Cobalt[1]	4.00	0.243	6.1	0.5	14
Copper[3]	1.00	0.112	11.2	3.4	53
Copper[1]	4.00	0.331	8.3	2.8	15
Iron[1]	4.40	0.260	5.8	2.3	16
Iron[3]	0.30	0.0495	16.5	0.6	43
Lead[1]	6.00	0.28	4.7	0.2	14
Magnesium[3]	0.20	0.021	10.5	6.3	42
Magnesium[1]	1.10	0.116	10.5	10.0	8
Manganese[1]	4.05	0.317	7.8	1.3	16
Manganese[3]	0.05	0.0068	13.5	6.0	14
Nickel[1]	3.93	0.383	9.8	2.0	14
Silver[3]	0.05	0.0088	17.5	10.6	7
Silver[1]	2.00	0.07	3.5	1.0	10
Sodium[1]	2.70	0.122	4.5	4.1	12
Strontium[1]	1.00	0.05	5.0	0.2	12
Zinc[3]	0.50	0.041	8.2	0.4	48
Extracted determination:					
Aluminum[2]	300	32	10.7	0.7	15
Beryllium[2]	5	1.7	34.0	20.0	9
Cadmium[3]	50	21.9	43.8	13.3	12
Cobalt[1]	300	28.5	9.5	1.0	6
Copper[1]	100	71.7	71.7	12.0	8
Iron[1]	250	19.0	7.6	3.6	4
Manganese[1]	21.5	2.4	11.2	7.4	8
Molybdenum[1]	9.5	1.1	11.6	1.3	5
Nickel[1]	56.8	15.2	26.8	13.6	14
Lead[3]	50	11.8	23.5	19.0	8
Silver[1]	5.2	1.4	26.9	3.0	7

* For direct determinations, mg/L; for extracted determinations, μg/L.
Superscripts refer to reference numbers.
Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing & Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

TABLE 3111:III. SINGLE-OPERATOR PRECISION AND RECOMMENDED CONTROL RANGES FOR ATOMIC ABSORPTION METHODS—DIRECT ASPIRATION AND EXTRACTED METALS

Metal	Conc.*	SD*	Relative SD %	No. of Participants	QC Std.*	Acceptable Range*
Direct determination:						
Aluminum[1]	4.50	0.23	5.1	15	5.00	4.3–5.7
Beryllium[1]	0.46	0.012	2.6	10	0.50	0.46–0.54
Calcium[1]	5.00	0.05	1.0	8	5.00	4.8–5.2
Chromium[1]	7.00	0.69	9.9	9	5.00	3.3–6.7
Cobalt[1]	4.00	0.21	5.3	14	4.00	3.4–4.6
Copper[1]	4.00	0.115	2.9	15	4.00	3.7–4.3
Iron[1]	5.00	0.19	3.8	16	5.00	4.4–5.6
Magnesium[1]	1.00	0.009	0.9	8	1.00	0.97–1.03
Nickel[4]	5.00	0.04	0.8	—	5.00	4.9–5.1
Silver[1]	2.00	0.25	12.5	10	2.00	1.2–2.8
Sodium[4]	8.2	0.1	1.2	—	5.00	4.8–5.2
Strontium[1]	1.00	0.04	4.0	12	1.00	0.87–1.13
Potassium[4]	1.6	0.2	12.5	—	1.6	1.0–2.2
Molybdenum[4]	7.5	0.07	0.9	—	10.0	9.7–10.3
Tin[4]	20.0	0.5	2.5	—	20.0	18.5–21.5
Titanium[4]	50.0	0.4	0.8	—	50.0	48.8–51.2
Vanadium	50.0	0.2	0.4	—	50.0	49.4–50.6
Extracted determination:						
Aluminum[1]	300	12	4.0	15	300	264–336
Cobalt[1]	300	20	6.7	6	300	220–380
Copper[1]	100	21	21	8	100	22–178
Iron[1]	250	12	4.8	4	250	180–320
Manganese[1]	21.5	202	10.2	8	25	17–23
Molybdenum[1]	9.5	1.0	10.5	5	10	5.5–14.5
Nickel[1]	56.8	9.2	16.2	14	50	22–78
Silver[1]	5.2	1.2	23.1	7	5.0	0.5–9.5

* For direct determinations, mg/L; for extracted determinations, µg/L.
Superscripts refer to reference numbers.
Source: AMERICAN SOCIETY FOR TESTING AND MATERIALS. 1986. Annual Book of ASTM Standards. Volume 11.01, Water and Environmental Technology. American Soc. Testing & Materials, Philadelphia, Pa. Copyright ASTM. Reprinted with permission.

vide lower sensitivity than single-element lamps. EDLs take a longer time to warm up and stabilize.

e. Pressure-reducing valves: Maintain supplies of fuel and oxidant at pressures somewhat higher than the controlled operating pressure of the instrument by using suitable reducing valves. Use a separate reducing valve for each gas.

f. Vent: Place a vent about 15 to 30 cm above the burner to remove fumes and vapors from the flame. This precaution protects laboratory personnel from toxic vapors, protects the instrument from corrosive vapors, and prevents flame stability from being affected by room drafts. A damper or variable-speed blower is desirable for modulating air flow and preventing flame disturbance. Select blower size to provide the air flow recommended by the instrument manufacturer. In laboratory locations with heavy particulate air pollution, use clean laboratory facilities (Section 3010C).

7. Quality Assurance/Quality Control

Some data typical of the precision and bias obtainable with the methods discussed are presented in Tables 3111:II and III.

Analyze a blank between sample or standard readings to verify baseline stability. Rezero when necessary.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 85 and 115%.

Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control. Recommended concentrations of standards to be run, limits of acceptability, and reported single-operator precision data are listed in Table 3111:III.

8. References

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3113 METALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

3113 A. Introduction

1. Applications

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection limits from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. This increase in sensitivity results from an increase in atom density within the furnace as compared to flame atomic absorption. Many elements can be determined at concentrations as low as 1.0 µg/L. An additional advantage of electrothermal atomic absorption is that only a very small volume of sample is required.

The electrothermal technique is used only at concentration levels below the optimum range of direct flame atomic absorption because it is subject to more interferences than the flame procedure and requires increased analysis time. The method of standard additions may be required to insure validity of data. Because of the high sensitivity of this technique, it is extremely susceptible to contamination; extra care in sample handling and analysis may be required.

2. Principle

Electrothermal atomic absorption spectroscopy is based on the same principle as direct flame atomization but an electrically heated atomizer or graphite furnace replaces the standard burner head. A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring, stage destroys organic matter and volatilizes other matrix components at an intermediate temperature. Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation. The inverse of the transmittance is related logarithmically to the absorbance, which is directly proportional to the number density of vaporized ground-state atoms (the Beer-Lambert law) over a limited concentration range.

3. Interferences

Electrothermal atomization determinations may be subject to significant interferences from molecular absorption as well as chemical and matrix effects. Molecular absorption may occur when components of the sample matrix volatilize during atomization, resulting in broadband absorption. Several background correction techniques are available commercially to compensate for this interference. A continuum source such as a deuterium arc can correct for background up to absorbance levels of about 0.8. Continuum lamp intensity diminishes at long wavelengths and use of continuum background correction is limited to analytical wavelengths below 350 nm. Zeeman effect background correctors can handle background absorbance up to 1.5 to 2.0. The Smith-Hieftje correction technique can accommodate background absorbance levels as large as 2.5 to 3.0 (see Section 3111A.3). Both Zeeman and Smith-Hieftje background corrections are susceptible to rollover (development of a negative absorbance-concentration relationship) at high absorbances. The rollover absorbance for each element should be available in the manufacturer's literature. Curvature due to rollover should become apparent during calibration; dilution produces a more lin-

* Approved by Standard Methods Committee, 1993.

ear calibration plot. Use background correction when analyzing samples containing high concentrations of acid or dissolved solids and in determining elements for which an absorption line below 350 nm is used.

Matrix modification can be useful in minimizing interference and increasing analytical sensitivity. Determine need for a modifier by evaluating recovery of a sample with a known addition. Recovery near 100% indicates that sample matrix does not affect analysis. Chemical modifiers generally modify relative volatilities of matrix and metal. Some modifiers enhance matrix removal, isolating the metal, while other modifiers inhibit metal volatilization, allowing use of higher ashing/charring temperatures and increasing efficiency of matrix removal. Chemical modifiers are added at high concentration (percent level) and can lead to sample contamination from impurities in the modifier solution. Heavy use of chemical modifiers may reduce the useful life (normally 50 to 100 firings) of the graphite tube. Some specific chemical modifiers and approximate concentrations are listed in Table 3113:I.

Addition of a chemical modifier directly to the sample before analysis is restricted to inexpensive additives (e.g. phosphoric acid). Use of palladium salts for matrix modification normally requires methods of co-addition, in which sample and modifier are added consecutively to the furnace either manually or, preferably, with an automatic sampler. Palladium salts (nitrate is preferred, chloride is acceptable) are listed in Table 3113:I as a modifier for many metals. The palladium solution (50 to 2000 mg/L) generally includes citric or ascorbic acid, which aids reduction of palladium in the furnace. Citric acid levels of 1 to 2% are typical. Use of hydrogen (5%) in the coolant gas (available commercially as a mixture) also reduces palladium, eliminating need for organic reducing acids. CAUTION: *Do not mix hydrogen and other gases in the laboratory; hydrogen gas is very flammable—handle with caution.* Use low levels of palladium (50 to 250 mg/L) for normal samples and higher levels for complex samples. Addition of excess palladium modifier may widen atomization peaks; in such cases peak area measurements may provide higher quality results. The recommended mode of modifier use is through co-addition to the furnace of about 10 µL of the palladium (or other) modifier solution. Palladium may not be the best modifier in all cases and cannot be recommended unconditionally. Test samples requiring a modifier first with palladium; test other modifiers only if palladium is unsuccessful or to minimize modifier cost. See Section 3113B.3 for preparation of modifier solution.

TABLE 3113:I. POTENTIAL MATRIX MODIFIERS FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY*

Modifier	Analyses for Which Modifier May Be Useful
1500 mg Pd/L + 1000 mg $Mg(NO_3)_2$/L[1]	Ag, As, Au, Bi, Cu, Ge, Mn, Hg, In, Sb, Se, Sn, Te, Tl
500–2000 mg Pd/L + reducing agent[2]†	Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb
5000 mg $Mg(NO_3)_2$/L[1]	Be, Co, Cr, Fe, Mn, V
100–500 mg Pd/L[2]	As, Ga, Ge, Sn
50 mg Ni/L[2]	As, Se, Sb
2% PO_4^{3-} + 1000 mg Mg $(NO_3)_2$/L[1]	Cd, Pb

*Assumes 10 µL modifier/10 µL sample.
†Citric acid (1–2%) preferred; ascorbic acid or H_2 acceptable.

Temperature ramping, i.e., gradual heating, can be used to decrease background interferences and permits analysis of samples with complex matrices. Ramping permits a controlled, continuous increase of furnace temperature in any of the various steps of the temperature sequence. Ramp drying is used for samples containing mixtures of solvents or for samples with a high salt content (to avoid spattering). If spattering is suspected, develop drying ramp by visual inspection of the drying stage, using a mirror. Samples that contain a complex mixture of matrix components sometimes require ramp charring to effect controlled, complete thermal decomposition. Ramp atomization may minimize background absorption by permitting volatilization of the element being determined before the matrix. This is especially applicable in the determination of such volatile elements as cadmium and lead. Use of time-resolved absorbance profiles (available on most modern instruments) greatly aids method development. Changes in atomization, notably the element peak appearance time and magnitude of background and metal absorbances, can be monitored directly.

Improve analysis by using a graphite platform, inserted into the graphite tube, as the atomization site. The platform is not heated as directly by the current flowing through the graphite tube; thus the metal atomizes later and under more uniform conditions.

Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added metal and that in the sample behave similarly under the specified conditions. [See Section 3113B.4*d*2)]. In the extreme, test every sample for recovery (85 to 115% recovery desired) to determine if standard addition is needed. Test every sample type for recovery. Recovery of only 40 to 85% generally indicates that standard addition is required. Often, as long as the samples are from sources of consistent properties, a representative recovery can be used to characterize the analysis and determine the necessity of standard addition. Test samples of unknown origin or of complex composition (digestates, for example) individually for metal recovery. Ideally, chemical modifiers and graphite platforms render the sample fit to be analyzed using a standard analytical calibration curve. Always verify this assumption; however, a properly developed method with judicious use of chemical modifiers should eliminate the necessity for standard addition in all but the most extreme samples.

Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem.

4. Sensitivity, Detection Limits, and Optimum Concentration Range

Estimated detection limits and optimum concentration ranges are listed in Table 3113:II. These values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions.

For a given sample, increased sensitivity may be achieved by using a larger sample volume or by reducing flow rate of the purge gas or by using gas interrupt during atomization. Note, however, that these techniques also will increase the effects of

TABLE 3113:II. DETECTION LEVELS AND CONCENTRATION RANGES FOR ELECTROTHERMAL ATOMIZATION ATOMIC ABSORPTION SPECTROMETRY

Element	Wavelength *nm*	Estimated Detection Limit *µg/L*	Optimum Concentration Range *µg/L*
Al	309.3	3	20–200
Sb	217.6	3	20–300
As	193.7	1	5–100
Ba	553.6	2	10–200
Be	234.9	0.2	1–30
Cd	228.8	0.1	0.5–10
Cr	357.9	2	5–100
Co	240.7	1	5–100
Cu	324.7	1	5–100
Fe	248.3	1	5–100
Pb*	283.3	1	5–100
Mn	279.5	0.2	1–30
Mo	313.3	1	3–60
Ni	232.0	1	5–100
Se	196.0	2	5–100
Ag	328.1	0.2	1–25
Sn	224.6	5	20–300

*The more sensitive 217.0-nm wavelength is recommended for instruments with background correction capabilities.

any interferences present. Sensitivity can be decreased by diluting the sample, reducing sample volume, increasing purge-gas flow, or using a less sensitive wavelength. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements and are recommended. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Using the Stabilized Temperature Platform Furnace (STPF) technique, which is a combination of individual techniques, also offers significant interference reduction with improved sensitivity. Sensitivity changes with sample tube age. Discard graphite tubes when significant variations in sensitivity or poor reproducibility are observed. The use of high acid concentrations, brine samples, and matrix modifiers often drastically reduces tube life. Preferably use the graphite platform in such situations.

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3113 B. Electrothermal Atomic Absorption Spectrometric Method

1. General Discussion

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin. It is also applicable to analysis of bismuth, gallium, germanium, gold, indium, mercury, tellurium, thallium, and vanadium, but precision and accuracy data are not yet available.

2. Apparatus

a. Atomic absorption spectrometer: See Section 3111A.6*a*. The instrument must have background correction capability.

b. Source lamps: See Section 3111A.6*d*.

c. Graphite furnace: Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Furnace heat con-

trollers with only three heating steps are adequate only for fresh waters with low dissolved solids content. For salt waters, brines, and other complex matrices, use a furnace controller with up to seven individually programmed heating steps. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with platforms to minimize interferences and to improve sensitivity.

d. Readout: See Section 3111A.6*c*.

e. Sample dispensers: Use microliter pipets (5 to 100 µL) or an automatic sampling device designed for the specific instrument.

f. Vent: See Section 3111A.6*f*.

g. Cooling water supply: Cool with tap water flowing at 1 to 4 L/min or use a recirculating cooling device.

h. Membrane filter apparatus: Use an all-glass filtering device and 0.45-µm or smaller-pore-diameter membrane filters. For trace analysis of aluminum, use polypropylene or TFE devices.

3. Reagents

a. Metal-free water: See Section 3111B.3*c*.

b. Hydrochloric acid, HCl, 1 + 1 and conc.

c. Nitric acid, HNO_3, 1 + 1 and conc.

d. Matrix modifier stock solutions:

1) *Magnesium nitrate*, 10 000 mg Mg/L: Dissolve 10.5 g $Mg(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

2) *Nickel nitrate*, 10 000 mg Ni/L: Dissolve 4.96 g $Ni(NO_3)_2 \cdot 6H_2O$ in water. Dilute to 100 mL.

3) *Phosphoric acid*, 10% (*v/v*): Add 10 mL conc H_3PO_4 to water. Dilute to 100 mL.

4) *Palladium nitrate*, 4000 mg Pd/L: Dissolve 8.89 g $Pd(NO_3)_2 \cdot H_2O$ in water. Dilute to 1 L.

5) *Citric acid*, 4%: Dissolve 40 g citric acid in water. Dilute to 1 L.

NOTE: All of the modifier solutions recommended in Table 3113:I can be prepared with volumetric combination of the above solutions and water. For preparation of other matrix modifiers, see references or follow manufacturers' instructions.

e. Stock metal solutions: Refer to Sections 3111B and 3114.

f. Chelating resin: 100 to 200 mesh* purified by heating at 60°C in 10*N* NaOH for 24 h. Cool resin and rinse 10 times each with alternating portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water.

g. Metal-free seawater (or brine): Fill a 1.4-cm-ID × 20-cm-long borosilicate glass column to within 2 cm of the top with purified chelating resin. Elute resin with successive 50-mL portions of 1*N* HCl, metal-free water, 1*N* NaOH, and metal-free water at the rate of 5 mL/min just before use. Pass salt water or brine through the column at a rate of 5 mL/min to extract trace metals present. Discard the first 10 bed volumes (300 mL) of eluate.

4. Procedures

a. Sample pretreatment: Before analysis, pretreat all samples as indicated below. Rinse all glassware with 1 + 1 HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

1) Dissolved metals—See Section 3030B. For samples requiring arsenic and/or selenium analysis add 3 mL 30% hydrogen peroxide/100 mL sample and an appropriate volume of nickel nitrate solution (see Table 3113:I) before analysis. For all other metals no further pretreatment is required except for adding an optional matrix modifier.

2) Total recoverable metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, and Sn)—NOTE: Sb and Sn are not recovered unless HCl is used in the digestion. See Section 3030D. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (see Table 3113:I), and dilute to volume with water.

3) Total recoverable metals (As, Se)—Transfer 100 mL of shaken sample, 1 mL conc HNO_3, and 2 mL 30% H_2O_2 to a clean, acid-washed 250-mL beaker. Heat on a hot plate without allowing solution to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 3113:I), and dilute to volume in a 100-mL volumetric flask with water. Substitution of palladium is uneconomical. Nickel may be deleted if palladium is co-added during analysis. Simultaneously prepare a digested blank by substituting water for sample and proceed with digestion as described above.

b. Instrument operation: Mount and align furnace device according to manufacturer's instructions. Turn on instrument and data collection system. Select appropriate light source and adjust to recommended electrical setting. Select proper wavelength and set all conditions according to manufacturer's instructions, including background correction. Background correction is important when elements are determined at short wavelengths or when sample has a high level of dissolved solids. Background correction normally is not necessary at wavelengths longer than 350 nm. If background correction above 350 nm is needed deuterium arc background correction is not useful and other types must be used.

Select proper inert- or sheath-gas flow. In some cases, it is desirable to interrupt the inert-gas flow during atomization. Such interruption results in increased sensitivity by increasing residence time of the atomic vapor in the optical path. Gas interruption also increases background absorption and intensifies interference effects, but modern background correction methods usually eliminate these problems. Consider advantages and disadvantages of this option for each matrix when optimizing analytical conditions.

To optimize graphite furnace conditions, carefully adjust furnace temperature settings to maximize sensitivity and precision and to minimize interferences. Follow manufacturer's instructions.

Use drying temperatures slightly above the solvent boiling point and provide enough time and temperature for complete evaporation without boiling or spattering.

Select atomization temperature by determining the lowest temperature providing maximum sensitivity without significantly eroding precision. Optimize by a series of successive determinations at various atomization temperatures using a standard solution giving an absorbance of 0.2 to 0.5.

The charring temperature must be high enough to maximize

* Chelex 100, or equivalent, available from Bio-Rad Laboratories, Richmond, Calif.

volatilization of interfering matrix components yet too low to volatilize the element of interest. With the drying and atomization temperatures set to their optimum values, analyze a standard solution at a series of charring temperatures in increasing increments of 50 to 100°C. When the optimum charring temperature is exceeded, there will be a significant drop in sensitivity. Plot charring temperature versus sample absorbance: the optimum charring temperature is the highest temperature without reduced sensitivity. Verify optimization with major changes in sample matrix.

c. Instrument calibration: Prepare standard solutions for instrument calibration by diluting metal stock solutions. Prepare standard solutions fresh daily.

Prepare a blank and at least three calibration standards in the appropriate concentration range (see Table 3113:II) for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In most cases, this simply requires matching the acid background of the samples. For seawaters or brines, however, use the metal-free matrix (¶ 3*g*) as the standard solution

TABLE 3113:III. INTERLABORATORY SINGLE-ANALYST PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Single-Analyst Precision % *RSD*					
Element	Concentration *μg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	66	108	70	—	—	66
	125	27	35	24	—	—	34
	11 000	11	—	—	22	—	—
	58 300	27	—	—	19	—	—
	460	9	—	—	—	30	—
	2 180	28	—	—	—	4	—
	10.5	20	13	13	13	56	18
	230	10	18	13	21	94	14
As	9.78	40	25	15	74	23	11
	227	10	6	8	11	15	6
Ba	56.5	36	21	29	59	23	27
	418	14	12	20	24	24	18
Be	0.45	18	27	15	30	2	11
	10.9	14	4	9	7	12	12
Cd	0.43	72	49	1	121	35	27
	12	11	17	22	14	11	15
Cr	9.87	24	33	10	23	15	10
	236	16	7	11	13	16	7
Co	29.7	10	17	10	19	24	12
	420	8	11	13	14	9	5
Cu	10.1	49	47	17	17	—	30
	234	8	15	6	21	—	11
	300	6	—	—	—	11	—
	1 670	11	—	—	—	6	—
Fe	26.1	144	52	153	—	—	124
	455	48	37	45	—	—	31
	1 030	17	—	—	30	—	—
	5 590	6	—	—	32	—	—
	370	14	—	—	—	19	—
	2 610	9	—	—	—	18	—
Pb	10.4	6	19	17	21	19	33
	243	17	7	17	18	12	16
Mn	0.44	187	180	—	—	—	275
	14.8	32	19	—	—	—	18
	91.0	15	—	—	48	—	—
	484.0	4	—	—	12	—	—
	111.0	12	—	—	—	21	—
	666.0	6	—	—	—	20	—
Ni	26.2	20	26	25	24	18	9
	461.0	15	11	9	8	11	4
Se	10.0	12	27	16	35	41	13
	235.0	6	6	15	6	13	14
Ag	8.48	10	—	—	15	27	16
	56.5	14	—	—	7	16	23
	0.45	27	166	48	—	—	—
	13.6	15	4	10	—	—	—

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diluent. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions.

Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision.

Construct an analytical curve by plotting the average peak absorbances or peak areas of the standard solution versus concentration on linear graph paper. Alternatively, use electronic instrument calibration if the instrument has this capability.

d. Sample analysis: Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of 85% to 115% for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of ≤ 10% is considered acceptable reproducibility. Average replicate values.

1) Direct determination—Inject a measured portion of pretreated sample into the graphite furnace. Use the same volume as was used to prepare the calibration curve. Usually add mod-

TABLE 3113:IV. INTERLABORATORY OVERALL PRECISION DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Overall Precision % *RSD*					
Element	Concentration *μg/L*	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28	99	114	124	—	—	131
	125	45	47	49	—	—	40
	11 000	19	—	—	43	—	—
	58 300	31	—	—	32	—	—
	460	20	—	—	—	47	—
	2 180	30	—	—	—	15	—
	10.5	37	19	22	50	103	39
	230	26	16	16	17	180	21
As	9.78	43	26	37	72	50	39
	227	18	12	13	20	15	14
Ba	56.5	68	38	43	116	43	65
	418	35	35	28	38	48	16
Be	0.45	28	31	15	67	50	35
	10.9	33	15	26	20	9	19
Cd	0.43	73	60	5	88	43	65
	12	19	25	41	26	20	27
Cr	9.87	30	53	24	60	41	23
	236	18	14	24	20	14	20
Co	29.7	13	26	17	18	21	17
	420	21	21	17	18	13	13
Cu	10.1	58	82	31	32	—	74
	234	12	33	19	21	—	26
	300	13	—	—	—	14	—
	1 670	12	—	—	—	13	—
Fe	26.1	115	93	306	—	—	204
	455	53	46	53	—	—	44
	1 030	32	—	—	25	—	—
	5 590	10	—	—	43	—	—
	370	28	—	—	—	22	—
	2 610	13	—	—	—	22	—
Pb	10.4	27	42	31	23	28	47
	243	18	19	17	19	19	25
Mn	0.44	299	272	—	—	—	248
	14.8	52	41	—	—	—	29
	91.0	16	—	—	45	—	—
	484.0	5	—	—	17	—	—
	111.0	15	—	—	—	17	—
	666.0	8	—	—	—	24	—
Ni	26.2	35	30	49	35	37	43
	461.0	23	22	15	12	21	17
Se	10.0	17	48	32	30	44	51
	235.0	16	18	18	17	22	34
Ag	8.48	23	—	—	16	35	34
	56.5	15	—	—	24	32	28
	0.45	57	90	368	—	—	—
	13.6	19	19	59	—	—	—

ifier immediately after the sample, preferably using an automatic sampler or a micropipet. Some methods require modifier to be injected before the sample. Use the same volume and concentration of modifier for all standards and samples. Dry, char, and atomize according to the preset program. Repeat until reproducible results are obtained.

Compare the average absorbance value or peak area to the calibration curve to determine concentration of the element of interest. Alternatively, read results directly if the instrument is equipped with this capability. If absorbance (or concentration) or peak area of the sample is greater than absorbance (concentration) or peak area of the most concentrated standard solution, dilute sample and reanalyze. If very large dilutions are required, another technique (e.g., flame AA or ICP) may be more suitable for this sample. Large dilution factors magnify small errors on final calculation. Keep acid background and concentration of matrix modifier (if present in the solutions) constant. Dilute the sample in a blank solution of acid and matrix modifiers.

TABLE 3113:V. INTERLABORATORY RELATIVE ERROR DATA FOR ELECTROTHERMAL ATOMIZATION METHODS[1]

		Relative Error %					
Element	Concentration µg/L	Lab Pure Water	Drinking Water	Surface Water	Effluent 1	Effluent 2	Effluent 3
Al	28.0	86	150	54	—	—	126
	125.0	4	41	39	—	—	30
	11 000.0	2	—	—	14	—	—
	58 300.0	12	—	—	7	—	—
	460.0	2	—	—	—	11	—
	2 180.0	11	—	—	—	9	—
Sb	10.5	30	32	28	24	28	36
	230.0	35	14	19	13	73	39
As	9.78	36	1	22	106	13	16
	227.0	3	7	10	19	6	13
Ba	56.5	132	54	44	116	59	40
	418.0	4	0	0	13	6	60
Be	0.45	40	16	11	16	10	15
	10.9	13	2	9	7	8	8
Cd	0.43	58	45	37	66	16	19
	12.0	4	6	5	22	18	3
Cr	9.87	10	9	4	2	5	15
	236.0	11	0	9	13	5	8
Co	29.7	7	7	1	6	3	13
	420.0	12	8	8	11	5	18
Cu	10.1	16	48	2	5	—	15
	234.0	8	7	0	4	—	19
	300.0	4	—	—	—	21	—
	1 670.0	6	—	—	—	2	—
Fe	26.1	85	60	379	—	—	158
	455.0	43	22	31	—	—	18
	1 030.0	8	—	—	8	—	—
	5 590.0	2	—	—	12	—	—
	370.0	4	—	—	—	11	—
	2 610.0	35	—	—	—	2	—
Pb	10.4	16	10	17	1	34	14
	243.0	5	15	8	18	15	29
Mn	0.44	332	304	—	—	—	556
	14.8	10	1	—	—	—	36
	91.0	31	—	—	10	—	—
	484.0	42	—	—	4	—	—
	111.0	1	—	—	—	29	—
	666.0	6	—	—	—	23	—
Ni	26.2	9	16	10	7	33	54
	461.0	15	19	18	31	16	18
Se	10.0	12	9	6	36	17	37
	235.0	7	7	0	13	10	17
Ag	8.48	12	—	—	1	51	20
	56.5	16	—	—	8	51	22
	0.45	34	162	534	—	—	—
	13.6	3	12	5	—	—	—

Freedom_0006095_0573

Proceed to ¶ 5*a* below.

2) Method of standard additions—Refer to ¶ 4*c* above. The method of standard additions is valid only when it falls in the linear portion of the calibration curve. Once instrument sensitivity has been optimized for the element of interest and the linear range for the element has been established, proceed with sample analyses.

Inject a measured volume of sample into furnace device. Dry, char or ash, and atomize samples according to preset program. Repeat until reproducible results are obtained. Record instrument response in absorbance or concentration as appropriate. Add a known concentration of the element of interest to a separate portion of sample so as not to change significantly the sample volume. Repeat the determination.

Add a known concentration (preferably twice that used in the first addition) to a separate sample portion. Mix well and repeat the determination.

Using linear graph paper, plot average absorbance or instrument response for the sample and the additions on the vertical axis against the concentrations of the added element on the horizontal axis, using zero as the concentration for the sample. Draw a straight line connecting the three points and extrapolate to zero absorbance. The intercept at the horizontal axis is the negative of the element concentration in the sample. The concentration axis to the left of the origin should be a mirror image of the axis to the right.

5. Calculations

a. Direct determination:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read directly from the instrument or from the calibration curve, µg/L, and
F = dilution factor.

b. Method of additions:

$$\mu g \text{ metal/L} = C \times F$$

where:

C = metal concentration as read from the method of additions plot, µg/L, and
F = dilution factor.

6. Precision and Bias

Data typical of the precision and bias obtainable are presented in Tables 3113:III, IV, and V.

7. Quality Control

See Section 3020 for specific quality control procedures to be followed during analysis. Although previous indications were that very low optimum concentration ranges were attainable for most metals (see Table 3113:II), data in Table 3113:III using variations of these protocols show that this may not be so. Exercise extreme care when applying this method to the lower concentration ranges. Verify analyst precision at the beginning of each analytical run by making triplicate analyses. Verify autosampler precision by checking volumes (by weight) delivered by the autosampler at routinely used injection volume settings.

8. Reference

1. COPELAND, T.R. & J.P. MANEY. 1986. EPA Method Study 31: Trace Metals by Atomic Absorption (Furnace Techniques). EPA-600/S4-85-070, U.S. Environmental Protection Agency, Environmental Monitoring and Support Lab., Cincinnati, Ohio.

9. Bibliography

RENSHAW, G.D. 1973. The determination of barium by flameless atomic absorption spectrophotometry using a modified graphite tube atomizer. *Atomic Absorption Newsletter* 12:158.

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PT analysis

INITIAL DEMONSTRATION OF CAPABILITY
Unknown Analysis - Data Summary

Method	200.8	Analyte	All Metals
SOP Number/Revision	Rev. 5.4	Date Completed	5/20/11

Instrument Name and Model Number	Perkin-Elmer ELAN 9000 ICP-MS
Instrument Software (version)	ELAN Version 3.4
Reason for Study	Analyst Validation
Source of Calibration Standards (Name/Lot #)	VHG SM23-100/009-0071
Quality Control Sample (Name/Lot #)	AccuStandard ICP-MS-QC2-1/210065074
Source of Unknown (Name/Lot#)	AccuStandard/IPE-MET-003A, Code# 372663-01-02
Date Unknown was Made	05/16/11
Date Sample and Quality Control was Digested	05/17/11
Date of Analysis	05/20/11

Replicate	Results	True Value	Percent Recovery	Acceptance Limits
Unknown	See Attachment			

Quality Control Recovery (% REC) = C_s / TV * 100

Where,

C_s = Result from quality control sample.

TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Carolyn Jannat Napier
Analyst

Gregory W Young 9-13-11
HHR Program Manager-Environmental Chemistry

8-13-12
HHR Program Manager-Quality Control Coordinator

Revision 2.0

INITIAL DEMONSTRATION OF CAPABILITY

Unknown - Data Summary

Analyst: Carolyn Napier CN

Concentration units: µg/L

Analyte (Mass)	True Value	Result	Percent Recovery	Vendor Acceptance Limits (µg/L)
Beryllium (9)	851	878	103.2%	724-961
Aluminum (27)	2200	2190	99.5%	1891-2492
Chromium (52)	750	786	104.8%	654-848
Cobalt (59)	667	719	107.8%	586-747
Nickel (60)	733	743	101.4%	661-820
Copper (63)	367	380	103.5%	331-404
Zinc (66)	333	327	98.2%	307-378
Arsenic (75)	583	646	110.8%	489-683
Selenium (82)	1733	1820	105.0%	1381-2005
Silver (107)	567	591	104.2%	487-649
Cadmium (111)	683	717	105.0%	583-776
Antimony (123)	417	382	91.6%	289-503
Barium (137)	1450	1500	103.4%	1235-1644
Thallium (205)	782	836	106.9%	631-906
Lead (208)	1550	1680	108.4%	1363-1729

Calibration Report

Unknown

Analyte	Mass	Curve Type	Slope	Intercept	Corr Coeff
Li	6.015	Linear Thru Zero	0.000000	0.000	0.000000
Be	9.012	Linear Thru Zero	0.002408	0.000	0.999996
Al	26.982	Linear Thru Zero	0.023609	0.000	1.000000
Sc	44.956	Linear Thru Zero	0.000000	0.000	0.000000
V	50.944	Linear Thru Zero	0.035679	0.000	0.999655
Cr	51.941	Linear Thru Zero	0.031558	0.000	0.999983
Cr	52.941	Linear Thru Zero	0.005419	0.000	0.978371
Mn	54.938	Linear Thru Zero	0.059487	0.000	0.998708
Co	58.933	Linear Thru Zero	0.038152	0.000	0.999997
Ni	59.933	Linear Thru Zero	0.008409	0.000	0.999993
Ni	61.928	Linear Thru Zero	0.001243	0.000	0.999996
Cu	62.930	Linear Thru Zero	0.018388	0.000	0.999997
Cu	64.928	Linear Thru Zero	0.008770	0.000	0.999997
Zn	65.926	Linear Thru Zero	0.005019	0.000	0.999986
Zn	66.927	Linear Thru Zero	0.000930	0.000	0.998230
Zn	67.925	Linear Thru Zero	0.003551	0.000	0.999981
Ge	71.922	Linear Thru Zero	0.000000	0.000	0.000000
As	74.922	Linear Thru Zero	0.005871	0.000	0.999997
Se	76.920	Linear Thru Zero	0.000462	0.000	0.998047
Se	81.917	Linear Thru Zero	0.000580	0.000	0.999992
Y	88.905	Linear Thru Zero	0.000000	0.000	0.000000
Mo	94.906	Linear Thru Zero	0.045157	0.000	0.993292
Mo	96.906	Linear Thru Zero	0.028236	0.000	0.992999
Mo	97.906	Linear Thru Zero	0.073145	0.000	0.993186
Ag	106.905	Linear Thru Zero	0.034579	0.000	0.999995
Ag	108.905	Linear Thru Zero	0.032767	0.000	0.999999
Cd	105.907	Linear Thru Zero	0.000803	0.000	0.999746
Cd	107.904	Linear Thru Zero	0.000610	0.000	0.999217
Cd	110.904	Linear Thru Zero	0.008095	0.000	0.999998
Cd	113.904	Linear Thru Zero	0.018475	0.000	0.999996
In	114.904	Linear Thru Zero	0.000000	0.000	0.000000
Sb	120.904	Linear Thru Zero	0.026514	0.000	0.999998
Sb	122.904	Linear Thru Zero	0.020339	0.000	0.999997
Ba	134.906	Linear Thru Zero	0.006968	0.000	0.999999
Ba	136.905	Linear Thru Zero	0.012056	0.000	0.999999
Tl	202.972	Linear Thru Zero	0.037253	0.000	0.999993
Tl	204.975	Linear Thru Zero	0.089196	0.000	0.999997
Pb	207.977	Linear Thru Zero	0.120963	0.000	0.999940
Bi	208.980	Linear Thru Zero	0.000000	0.000	0.000000
Na	22.990	Linear Thru Zero	0.022592	0.000	0.983181
Mg	23.985	Linear Thru Zero	0.015199	0.000	0.999918
K	38.964	Linear Thru Zero	0.036010	0.000	0.988395
Ca	43.956	Linear Thru Zero	0.001162	0.000	0.995965
Fe	53.940	Linear Thru Zero	0.002969	0.000	0.999868
Sc	44.956	Linear Thru Zero	0.000000	0.000	0.000000
Kr	82.914	Linear Thru Zero	0.000000	0.000	0.000000
Ru	98.906	Linear Thru Zero	0.000000	0.000	0.000000
Pd	104.905	Linear Thru Zero	0.000000	0.000	0.000000
Sn	117.902	Linear Thru Zero	0.000000	0.000	0.000000
Br	80.916	Linear Thru Zero	0.000000	0.000	0.000000

G4

Run List

Sample File Name: 052011b.sam

AS Loc.	Sample ID	Batch Index	Sample Type	Method
2	blank		Blank	drinkingwater200_8_no_sc_is.mth
3	cal std 1		Standard	drinkingwater200_8_no_sc_is.mth
4	cal std 2		Standard	drinkingwater200_8_no_sc_is.mth
5	cal std 3		Standard	drinkingwater200_8_no_sc_is.mth
6	cal std 4		Standard	drinkingwater200_8_no_sc_is.mth
2	Blank	1	Sample	drinkingwater200_8_no_sc_is.mth
5	ICV	2	Sample	drinkingwater200_8_no_sc_is.mth
2	Blank	3	Sample	drinkingwater200_8_no_sc_is.mth
7	QCS	4	Sample	drinkingwater200_8_no_sc_is.mth
9	LRB	5	Sample	drinkingwater200_8_no_sc_is.mth
10	MRL 1ppb	6	Sample	drinkingwater200_8_no_sc_is.mth
11	MRL 10ppb	7	Sample	drinkingwater200_8_no_sc_is.mth
12	LFB	8	Sample	drinkingwater200_8_no_sc_is.mth
13	UNK 50X	9	Sample	drinkingwater200_8_no_sc_is.mth
14	UNK DDP 50X	10	Sample	drinkingwater200_8_no_sc_is.mth
15	UNK LFM 50X	11	Sample	drinkingwater200_8_no_sc_is.mth
16	UNK-LFMD 50X	12	Sample	drinkingwater200_8_no_sc_is.mth
17	UNK 10X	13	Sample	drinkingwater200_8_no_sc_is.mth
18	UNK DDP 10X	14	Sample	drinkingwater200_8_no_sc_is.mth
19	UNK LFM 10X	15	Sample	drinkingwater200_8_no_sc_is.mth
20	UNK LFMD 10X	16	Sample	drinkingwater200_8_no_sc_is.mth
5	CCV	17	Sample	drinkingwater200_8_no_sc_is.mth
2	Blank	18	Sample	drinkingwater200_8_no_sc_is.mth

Freedom_0006095_0578

Daily Performance Report

Sample ID: Daily Performance Check
Sample Date/Time: Friday, May 20, 2011 13:43:26
Sample Description:
Method File: C:\Elandata\Method\200.8 Methods\EPA2008 DAILY.mth
Dataset File: C:\Elandata\DataSet\Data\Daily Performance Check.1685
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Dual Detector Mode: Dual

Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

	Analyte	Mass	Meas. Intens. Mean	Net Intens. Mean	Net Intens. SD	Net Intens. RSD
	Be	9.0	11461.6	11461.623	222.293	1.9
	Mg	24.0	81422.7	81422.664	1162.567	1.4
	Co	58.9	224315.6	224315.572	2366.909	1.1
	Rh	102.9	386477.8	386477.795	1575.701	0.4
	In	114.9	451478.9	451478.867	1377.557	0.3
	Pb	208.0	199520.6	199520.582	1392.792	0.7
⌈>	Ba	137.9	363813.9	363813.891	1308.689	0.4
⌊	Ba++	69.0	7110.0	0.020	0.000	1.9
⌈>	Ce	139.9	444052.9	444052.907	2188.637	0.5
⌊	CeO	155.9	11261.6	0.025	0.001	2.6
	Bkgd	220.0	20.4	20.400	6.950	34.1
	Kr	83.9	1983.9	1983.890	40.697	2.1
	C	12.0	1507528.2	1507528.165	12072.616	0.8

Current Optimization File Data

Current Value	Description
0.85	Nebulizer Gas Flow
5.50	Lens Voltage
1000.00	ICP RF Power
-1550.00	Analog Stage Voltage
750.00	Pulse Stage Voltage
23.00	Discriminator Threshold
-2.00	AC Rod Offset

Current Autolens Data

Analyte	Mass	Num of Pts	DAC Value	Maximum Intensity
Be	9	45	5.5	11122.3
Co	59	45	6.0	229744.8
In	115	45	7.0	456018.6
U	238	45	9.0	438541.4

Freedom_0006095_0579

SmartTune Wizard - Summary

Optimization Summary

SmartTune file: C:\Elandata\Wizard\SmartTune\2008 SmartTune Daily.swz

Start Time: 5/20/2011 1:29:12 PM
End Time: 5/20/2011 1:45:05 PM

Mass Calibration and Resolution - [Passed] Optimum value(s): N/A
Target/Obtained mass (3.016/2.975), Target/Obtained resolution (0.65/0.639)
Target/Obtained mass (9.0122/8.975), Target/Obtained resolution (0.65/0.651)
Target/Obtained mass (23.985/24.025), Target/Obtained resolution (0.65/0.660)
Target/Obtained mass (58.9332/58.975), Target/Obtained resolution (0.65/0.641)
Target/Obtained mass (102.905/102.925), Target/Obtained resolution (0.65/0.653)
Target/Obtained mass (114.904/114.925), Target/Obtained resolution (0.65/0.653)
Target/Obtained mass (207.977/207.975), Target/Obtained resolution (0.65/0.648)
Target/Obtained mass (238.05/238.025), Target/Obtained resolution (0.65/0.650)

Nebulizer Gas Flow - [Passed] Optimum value(s): 0.85
Obtained Intensity (Rh 102.905): 136983
Obtained Formula (CeO 155.9 / Ce 139.905): 0.026 (=3099 / 119590)

AutoLens - [Passed] Optimum value(s): y = 0.016 x + 5.227

Daily Performance Check - [Passed] Optimum value(s): N/A
Obtained Intensity (Mg 23.985): 81423
Obtained Intensity (Rh 102.905): 386478
Obtained Intensity (In 114.904): 451479
Obtained Intensity (Pb 207.977): 199521
Obtained Intensity (Bkgd 220): 20
Obtained Formula (Ba++ 68.9525 / Ba 137.905): 0.020 (=7110 / 363814)
Obtained Formula (CeO 155.9 / Ce 139.905): 0.025 (=11262 / 444053)

Freedom_0006095_0580

SmartTune Wizard - Details

Optimization Details

SmartTune file: C:\Elandata\Wizard\SmartTune\2008 SmartTune Daily.swz

Optimization Status

Start Time: 5/20/2011 1:29:12 PM

Mass Calibration and Resolution

Optimization Settings:

Method: C:\Elandata\Method\200.8 Methods\EPA2008 TUNING.mth.
Tuning File: C:\Elandata\Tuning\EPA.tun
Iterations: 6
Target accuracy (+/- amu): 0.05 for Mass Cal. and 0.1 for Resolution
Peak height (%) for Res. Opt.: 10

Optimization Results:

Initial Try

Target/Obtained mass (3.016/3.025), Target/Obtained resolution (0.65/0.649)
Target/Obtained mass (9.0122/9.075), Target/Obtained resolution (0.65/0.672) - <Target not achieve
Target/Obtained mass (23.985/23.975), Target/Obtained resolution (0.65/0.679)
Target/Obtained mass (58.9332/58.925), Target/Obtained resolution (0.65/0.674)
Target/Obtained mass (102.905/102.925), Target/Obtained resolution (0.65/0.672)
Target/Obtained mass (114.904/114.925), Target/Obtained resolution (0.65/0.669)
Target/Obtained mass (207.977/207.975), Target/Obtained resolution (0.65/0.670)
Target/Obtained mass (238.05/238.075), Target/Obtained resolution (0.65/0.665)
[Failed]

Retry 1

Target/Obtained mass (3.016/2.975), Target/Obtained resolution (0.65/0.639)
Target/Obtained mass (9.0122/8.975), Target/Obtained resolution (0.65/0.651)
Target/Obtained mass (23.985/24.025), Target/Obtained resolution (0.65/0.660)
Target/Obtained mass (58.9332/58.975), Target/Obtained resolution (0.65/0.641)
Target/Obtained mass (102.905/102.925), Target/Obtained resolution (0.65/0.653)
Target/Obtained mass (114.904/114.925), Target/Obtained resolution (0.65/0.653)
Target/Obtained mass (207.977/207.975), Target/Obtained resolution (0.65/0.648)
Target/Obtained mass (238.05/238.025), Target/Obtained resolution (0.65/0.650)

[Passed] Optimum value(s): N/A

Nebulizer Gas Flow

Optimization Settings:

Method: C:\Elandata\Method\200.8 Methods\EPA2008 OPTIMIZE.mth.
Initial Try - Start/End/Step: 0.75/1.1/0.02.
Intensity Criterion: Rh 102.905 Maximum
Formula Criterion: CeO 155.9 / Ce 139.905 <= 0.026

Optimization Results:

Initial Try

Obtained Intensity (Rh 102.905): 136983
Obtained Formula (CeO 155.9 / Ce 139.905): 0.026 (=3099 / 119590)

[Passed] Optimum value(s): 0.85

AutoLens

Optimization Settings:

Method: C:\Elandata\Method\200.8 Methods\DrinkingWaterAutoLens Calibration.mth.
Initial Try - Start/End/Step: 2/13/0.25.

Optimization Results:

Initial Try

Freedom_0006095_0581

[Passed] Optimum value(s): y = 0.016 x + 5.227

Analyte	Mass	Points	DAC	MaxIntensity
Be	9.012	45	5.5	11122.3
Co	58.933	45	6	229745
In	114.904	45	7	456019
U	238.05	45	9	438541

Daily Performance Check

Optimization Settings:

Method: C:\Elandata\Method\200.8 Methods\EPA2008 DAILY.mth.
Intensity Criterion: Mg 23.985 > 40000
Intensity Criterion: Rh 102.905 > 150000
Intensity Criterion: In 114.904 > 300000
Intensity Criterion: Pb 207.977 > 100000
Intensity Criterion: Bkgd 220 <= 30
Formula Criterion: Ba++ 68.9525 / Ba 137.905 <= 0.03
Formula Criterion: CeO 155.9 / Ce 139.905 <= 0.03

Optimization Results:

Initial Try

Obtained Intensity (Mg 23.985): 81423
Obtained Intensity (Rh 102.905): 386478
Obtained Intensity (In 114.904): 451479
Obtained Intensity (Pb 207.977): 199521
Obtained Intensity (Bkgd 220): 20
Obtained Formula (Ba++ 68.9525 / Ba 137.905): 0.020 (=7110 / 363814)
Obtained Formula (CeO 155.9 / Ce 139.905): 0.025 (=11262 / 444053)

[Passed] Optimum value(s): N/A

End Time: 5/20/2011 1:45:05 PM

Freedom_0006095_0582

Quantitative Analysis - Summary Report

Sample ID: blank

Sample Date/Time: Friday, May 20, 2011 13:53:21
Sample Description:
Solution Type: Blank
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\blank.1686
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈>	Li	6	419192	1.694		
|	Be	9	17	11.245		
⌊	Al	27	8657	0.338		
	Sc	45	441159	2.191		
⌈	V	51	-33726	19.231		
|	Cr	52	32768	3.966		
|	Cr	53	348182	7.828		
|	Mn	55	4559	0.876		
|	Co	59	81	6.188		
|	Ni	60	63	22.892		
|	Ni	62	122	6.025		
|	Cu	63	273	1.597		
|	Cu	65	209	4.349		
|	Zn	66	2008	2.195		
|	Zn	67	8119	18.535		
|	Zn	68	1050	8.928		
|>	Ge	72	506936	1.335		
|	As	75	-1640	18.549		
|	Se	77	11511	4.487		
⌊	Se	82	61	14.181		
⌈>	Y	89	270431	0.598		
|	Mo	95	53	11.477		
|	Mo	97	106	3.042		
⌊	Mo	98	31	11.067		
⌈	Ag	107	165	8.290		
|	Ag	109	158	3.807		
|	Cd	106	-2157	4.008		
|	Cd	108	-2316	3.298		
|	Cd	111	284	7.166		

Freedom_0006095_0583

	Cd	114	231	35.854
>	In	115	399488	1.002
	Sb	121	673	16.561
	Sb	123	526	14.841
	Ba	135	73	12.712
	Ba	137	112	17.292
	Tl	203	417	2.400
	Tl	205	982	0.713
	Pb	208	1505	6.243
>	Bi	209	276944	0.692
	Na	23	22459	2.393
	Mg	24	1019	3.136
	K	39	1084511	0.460
	Ca	44	92085	0.662
	Fe	54	75753	0.596
>	Sc	45	441159	2.191
	Kr	83	444	3.077
	Ru	99	22	24.052
	Pd	105	1982	3.101
	Sn	118	2077	21.323
	Br	81	36513	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
>	Li	6					ug/L
	Be	9					ug/L
	Al	27					ug/L
	Sc	45					ug/L
	V	51					ug/L
	Cr	52					ug/L
	Cr	53					ug/L
	Mn	55					ug/L
	Co	59					ug/L
	Ni	60					ug/L
	Ni	62					ug/L
	Cu	63					ug/L
	Cu	65					ug/L
	Zn	66					ug/L
	Zn	67					ug/L
	Zn	68					ug/L
>	Ge	72					ug/L
	As	75					ug/L
	Se	77					ug/L
	Se	82					ug/L
>	Y	89					ug/L
	Mo	95					ug/L
	Mo	97					ug/L
	Mo	98					ug/L
	Ag	107					ug/L
	Ag	109					ug/L
	Cd	106					ug/L
	Cd	108					ug/L
	Cd	111					ug/L

Freedom_0006095_0584

	Cd	114	ug/L
>	In	115	ug/L
	Sb	121	ug/L
	Sb	123	ug/L
	Ba	135	ug/L
	Ba	137	ug/L
	Tl	203	ug/L
	Tl	205	ug/L
	Pb	208	ug/L
>	Bi	209	ug/L
	Na	23	ug/L
	Mg	24	ug/L
	K	39	ug/L
	Ca	44	ug/L
	Fe	54	ug/L
>	Sc	45	ug/L
	Kr	83	ug/L
	Ru	99	ug/L
	Pd	105	ug/L
	Sn	118	ug/L
	Br	81	ug/L

Quantitative Analysis - Summary Report

Sample ID: cal std 1

Sample Date/Time: Friday, May 20, 2011 13:57:57
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 1.1687
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	427971	1.482	419191.962	1.694
	Be	9	1041	2.983	16.833	11.245
	Al	27	17157	1.321	8656.786	0.338
	Sc	45	444230	1.387	441159.124	2.191
	V	51	-13262	20.281	-33725.922	19.231
	Cr	52	52236	0.915	32767.677	3.966
	Cr	53	405209	1.438	348181.626	7.828
	Mn	55	39704	2.483	4559.455	0.876
	Co	59	20593	1.784	81.334	6.188
	Ni	60	5485	1.219	63.000	22.892
	Ni	62	947	1.819	122.334	6.025
	Cu	63	11698	3.316	273.004	1.597
	Cu	65	5592	2.926	208.669	4.349
	Zn	66	5379	0.475	2007.555	2.195
	Zn	67	11129	5.249	8119.374	18.535
	Zn	68	3531	2.141	1050.394	8.928
>	Ge	72	516437	0.243	506936.298	1.335
	As	75	1382	7.552	-1639.760	18.549
	Se	77	13150	0.435	11511.293	4.487
	Se	82	356	18.002	60.571	14.181
>	Y	89	204822	0.640	270431.466	0.598
	Mo	95	5739	1.340	53.000	11.477
	Mo	97	3579	1.345	105.667	3.042
	Mo	98	8956	0.753	30.629	11.067
	Ag	107	14158	1.416	164.668	8.290
	Ag	109	13328	0.497	158.335	3.807
	Cd	106	-1280	3.433	-2157.317	4.008
	Cd	108	-1481	3.319	-2316.105	3.298
	Cd	111	3408	2.526	283.644	7.166

Freedom_0006095_0586

Cd	114	7587	1.637	230.623	35.854
> In	115	399686	0.565	399487.744	1.002
Sb	121	12684	0.314	673.025	16.561
Sb	123	9725	2.050	525.666	14.841
Ba	135	2915	0.859	72.667	12.712
Ba	137	5091	1.285	112.334	17.292
Tl	203	10795	1.494	417.343	2.400
Tl	205	25842	1.835	982.053	0.713
Pb	208	36294	1.090	1504.716	6.243
> Bi	209	280491	0.305	276943.547	0.692
Na	23	241710	2.340	22459.386	2.393
Mg	24	11106	3.026	1018.724	3.136
K	39	1382930	1.077	1084510.719	0.460
Ca	44	93862	0.242	92085.044	0.662
Fe	54	78514	1.840	75752.787	0.596
> Sc	45	444230	1.387	441159.124	2.191
Kr	83	443	4.198	443.677	3.077
Ru	99	27	5.728	22.000	24.052
Pd	105	1469	1.728	1981.883	3.101
Sn	118	1141	9.642	2076.911	21.323
Br	81	37466	0.782	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	427971.310				ug/L
	Be	9	0.002	1.000	0.04	3.6	ug/L
	Al	27	0.019				ug/L
	Sc	45	3070.685				ug/L
	V	51	0.041	1.000	0.13	12.7	ug/L
	Cr	52	0.037	1.000	0.03	2.7	ug/L
	Cr	53	0.098	1.000	0.12	12.3	ug/L
	Mn	55	0.068	1.000	0.03	2.8	ug/L
	Co	59	0.040	1.000	0.02	1.8	ug/L
	Ni	60	0.010	1.000	0.01	1.4	ug/L
	Ni	62	0.002	1.000	0.02	2.2	ug/L
	Cu	63	0.022	1.000	0.03	3.3	ug/L
	Cu	65	0.010	1.000	0.03	3.1	ug/L
	Zn	66	0.006	1.000	0.00	0.4	ug/L
	Zn	67	0.006	1.000	0.21	20.9	ug/L
	Zn	68	0.005	1.000	0.03	3.4	ug/L
>	Ge	72	516437.493				ug/L
	As	75	0.006	1.000	0.03	3.3	ug/L
	Se	77	0.003	1.000	0.04	4.3	ug/L
	Se	82	0.001	1.000	0.22	21.6	ug/L
>	Y	89	204822.055				ug/L
	Mo	95	0.028	1.000	0.01	1.5	ug/L
	Mo	97	0.017	1.000	0.01	1.0	ug/L
	Mo	98	0.044	1.000	0.01	1.2	ug/L
	Ag	107	0.035	1.000	0.01	0.9	ug/L
	Ag	109	0.033	1.000	0.01	0.6	ug/L
	Cd	106	0.002	1.000	0.04	4.2	ug/L
	Cd	108	0.002	1.000	0.05	4.9	ug/L
	Cd	111	0.008	1.000	0.02	2.4	ug/L

|	Cd	114	0.018	**1.000**	0.02	2.2	ug/L
|>	In	115	399686.395				ug/L
|	Sb	121	0.030	**1.000**	0.01	0.9	ug/L
|	Sb	123	0.023	**1.000**	0.02	1.9	ug/L
|	Ba	135	0.007	**1.000**	0.01	1.2	ug/L
|	Ba	137	0.012	**1.000**	0.01	0.8	ug/L
|	Tl	203	0.037	**1.000**	0.02	1.9	ug/L
|	Tl	205	0.089	**1.000**	0.02	1.6	ug/L
|	Pb	208	0.124	**1.000**	0.01	1.5	ug/L
|>	Bi	209	280490.747				ug/L
|	Na	23	0.493	**1.000**	0.04	4.0	ug/L
|	Mg	24	0.023	**1.000**	0.03	3.1	ug/L
|	K	39	0.655	**1.000**	0.03	3.4	ug/L
|	Ca	44	0.003	**1.000**	1.30	129.6	ug/L
|	Fe	54	0.005	**1.000**	0.54	53.6	ug/L
|>	Sc	45	444229.808				ug/L
	Kr	83	-0.333				ug/L
	Ru	99	4.667				ug/L
	Pd	105	-512.431				ug/L
	Sn	118	-935.839				ug/L
	Br	81	953.536				ug/L

Freedom_0006095_0588

Quantitative Analysis - Summary Report

Sample ID: cal std 2
Sample Date/Time: Friday, May 20, 2011 14:02:34
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 2.1688
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	424989	1.600	419191.962	1.694
	Be	9	10136	0.699	16.833	11.245
	Al	27	109039	2.186	8656.786	0.338
	Sc	45	453316	1.389	441159.124	2.191
	V	51	155686	5.819	-33725.922	19.231
	Cr	52	199470	1.557	32767.677	3.966
	Cr	53	428403	1.763	348181.626	7.828
	Mn	55	340086	2.303	4559.455	0.876
	Co	59	197834	0.878	81.334	6.188
	Ni	60	42428	1.054	63.000	22.892
	Ni	62	6537	1.867	122.334	6.025
	Cu	63	94906	1.152	273.004	1.597
	Cu	65	45708	1.153	208.669	4.349
	Zn	66	27334	1.255	2007.555	2.195
	Zn	67	15193	4.309	8119.374	18.535
	Zn	68	19332	0.377	1050.394	8.928
>	Ge	72	520947	0.650	506936.298	1.335
	As	75	28183	1.346	-1639.760	18.549
	Se	77	15242	1.966	11511.293	4.487
	Se	82	3067	0.416	60.571	14.181
>	Y	89	183644	1.237	270431.466	0.598
	Mo	95	54851	0.176	53.000	11.477
	Mo	97	34497	1.163	105.667	3.042
	Mo	98	88544	0.645	30.629	11.067
	Ag	107	136856	0.206	164.668	8.290
	Ag	109	129314	1.349	158.335	3.807
	Cd	106	1507	7.922	-2157.317	4.008
	Cd	108	657	17.627	-2316.105	3.298
	Cd	111	31970	0.753	283.644	7.166

Freedom_0006095_0589

Cd	114	73124	1.054	230.623	35.854
> In	115	397564	0.620	399487.744	1.002
Sb	121	107308	0.992	673.025	16.561
Sb	123	81145	0.206	525.666	14.841
Ba	135	27718	0.457	72.667	12.712
Ba	137	47927	0.895	112.334	17.292
Tl	203	104602	1.241	417.343	2.400
Tl	205	250509	1.952	982.053	0.713
Pb	208	339772	0.395	1504.716	6.243
> Bi	209	276957	0.279	276943.547	0.692
Na	23	123057	0.918	22459.386	2.393
Mg	24	68852	2.580	1018.724	3.136
K	39	1258032	0.202	1084510.719	0.460
Ca	44	95539	0.624	92085.044	0.662
Fe	54	90076	0.650	75752.787	0.596
> Sc	45	453316	1.389	441159.124	2.191
Kr	83	427	1.171	443.677	3.077
Ru	99	25	32.149	22.000	24.052
Pd	105	1358	3.606	1981.883	3.101
Sn	118	733	6.873	2076.911	21.323
Br	81	37611	1.063	36512.847	0.653

Concentration Results

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
> Li	6	424988.526				ug/L
Be	9	0.024	**9.999**	0.09	0.9	ug/L
Al	27	0.236	**10.000**	0.07	0.7	ug/L
Sc	45	12156.520				ug/L
V	51	0.365	**9.988**	0.50	5.0	ug/L
Cr	52	0.318	**9.985**	0.26	2.6	ug/L
Cr	53	0.136	**9.420**	0.96	10.2	ug/L
Mn	55	0.644	**9.995**	0.30	3.0	ug/L
Co	59	0.380	**9.995**	0.05	0.5	ug/L
Ni	60	0.081	**9.971**	0.15	1.6	ug/L
Ni	62	0.012	**9.971**	0.20	2.0	ug/L
Cu	63	0.182	**9.979**	0.16	1.6	ug/L
Cu	65	0.087	**9.981**	0.18	1.8	ug/L
Zn	66	0.049	**9.967**	0.20	2.0	ug/L
Zn	67	0.013	**9.692**	0.83	8.6	ug/L
Zn	68	0.035	**9.964**	0.05	0.5	ug/L
> Ge	72	520946.840				ug/L
As	75	0.057	**9.997**	0.07	0.7	ug/L
Se	77	0.007	**9.692**	0.67	6.9	ug/L
Se	82	0.006	**10.001**	0.10	1.0	ug/L
> Y	89	183643.508				ug/L
Mo	95	0.299	**10.007**	0.11	1.1	ug/L
Mo	97	0.187	**10.009**	0.11	1.1	ug/L
Mo	98	0.482	**10.009**	0.09	0.9	ug/L
Ag	107	0.344	**9.998**	0.07	0.7	ug/L
Ag	109	0.325	**9.999**	0.12	1.2	ug/L
Cd	106	0.009	**9.864**	0.33	3.3	ug/L
Cd	108	0.007	**9.824**	0.39	3.9	ug/L
Cd	111	0.080	**10.002**	0.04	0.4	ug/L

Freedom_0006095_0590

	Cd	114	0.183	**10.000**	0.05	0.5	ug/L
>	In	115	397563.805				ug/L
	Sb	121	0.268	**9.988**	0.10	1.0	ug/L
	Sb	123	0.203	**9.987**	0.08	0.8	ug/L
	Ba	135	0.070	**9.998**	0.09	0.9	ug/L
	Ba	137	0.120	**9.996**	0.13	1.3	ug/L
	Tl	203	0.376	**10.002**	0.12	1.2	ug/L
	Tl	205	0.901	**10.002**	0.22	2.2	ug/L
	Pb	208	1.221	**9.999**	0.07	0.7	ug/L
>	Bi	209	276957.179				ug/L
	Na	23	0.221	**8.254**	0.18	2.2	ug/L
	Mg	24	0.150	**9.949**	0.31	3.1	ug/L
	K	39	0.317	**8.371**	0.90	10.7	ug/L
	Ca	44	0.002	**8.964**	11.29	126.0	ug/L
	Fe	54	0.027	**9.915**	0.99	10.0	ug/L
>	Sc	45	453315.644				ug/L
	Kr	83	-16.667				ug/L
	Ru	99	3.333				ug/L
	Pd	105	-624.115				ug/L
	Sn	118	-1343.548				ug/L
	Br	81	1097.799				ug/L

Quantitative Analysis - Summary Report

Sample ID: cal std 3
Sample Date/Time: Friday, May 20, 2011 14:07:12
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 3.1689
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	426347	0.923	419191.962	1.694
	Be	9	51060	0.375	16.833	11.245
	Al	27	511412	0.523	8656.786	0.338
	Sc	45	452038	1.586	441159.124	2.191
	V	51	933676	3.304	-33725.922	19.231
	Cr	52	856075	1.125	32767.677	3.966
	Cr	53	508713	1.435	348181.626	7.828
	Mn	55	1692101	1.144	4559.455	0.876
	Co	59	988620	1.295	81.334	6.188
	Ni	60	216592	1.680	63.000	22.892
	Ni	62	32234	1.614	122.334	6.025
	Cu	63	473008	0.871	273.004	1.597
	Cu	65	227050	1.772	208.669	4.349
	Zn	66	130542	2.406	2007.555	2.195
	Zn	67	32861	2.955	8119.374	18.535
	Zn	68	93579	1.720	1050.394	8.928
>	Ge	72	515594	1.234	506936.298	1.335
	As	75	149947	1.589	-1639.760	18.549
	Se	77	24122	0.808	11511.293	4.487
	Se	82	15139	1.120	60.571	14.181
>	Y	89	99308	0.163	270431.466	0.598
	Mo	95	275441	0.807	53.000	11.477
	Mo	97	173015	0.801	105.667	3.042
	Mo	98	446801	0.467	30.629	11.067
	Ag	107	694797	1.249	164.668	8.290
	Ag	109	655780	1.869	158.335	3.807
	Cd	106	14196	0.349	-2157.317	4.008
	Cd	108	10493	1.488	-2316.105	3.298
	Cd	111	162288	0.932	283.644	7.166

Freedom_0006095_0592

Cd	114	371149	0.602	230.623	35.854
> In	115	399392	1.145	399487.744	1.002
Sb	121	528715	0.443	673.025	16.561
Sb	123	408216	0.729	525.666	14.841
Ba	135	139614	0.434	72.667	12.712
Ba	137	240226	0.691	112.334	17.292
Tl	203	520357	0.979	417.343	2.400
Tl	205	1230488	0.886	982.053	0.713
Pb	208	1713858	0.723	1504.716	6.243
> Bi	209	277098	1.383	276943.547	0.692
Na	23	526457	0.583	22459.386	2.393
Mg	24	336300	0.991	1018.724	3.136
K	39	1937884	0.520	1084510.719	0.460
Ca	44	118101	0.253	92085.044	0.662
Fe	54	143025	1.606	75752.787	0.596
> Sc	45	452038	1.586	441159.124	2.191
Kr	83	433	4.351	443.677	3.077
Ru	99	60	14.097	22.000	24.052
Pd	105	765	4.208	1981.883	3.101
Sn	118	554	5.683	2076.911	21.323
Br	81	38286	0.497	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	426346.738				ug/L
	Be	9	0.120	**50.011**	0.43	0.9	ug/L
	Al	27	1.179	**49.999**	0.54	1.1	ug/L
	Sc	45	10878.935				ug/L
	V	51	1.877	**50.050**	1.25	2.5	ug/L
	Cr	52	1.596	**50.002**	0.27	0.5	ug/L
	Cr	53	0.300	**47.424**	1.89	4.0	ug/L
	Mn	55	3.273	**50.031**	0.48	1.0	ug/L
	Co	59	1.917	**50.019**	0.62	1.2	ug/L
	Ni	60	0.420	**50.056**	0.86	1.7	ug/L
	Ni	62	0.062	**50.018**	0.56	1.1	ug/L
	Cu	63	0.917	**50.014**	0.75	1.5	ug/L
	Cu	65	0.440	**50.011**	0.58	1.2	ug/L
	Zn	66	0.249	**50.046**	0.60	1.2	ug/L
	Zn	67	0.048	**49.195**	1.17	2.4	ug/L
	Zn	68	0.179	**50.039**	0.25	0.5	ug/L
>	Ge	72	515594.237				ug/L
	As	75	0.294	**50.048**	0.58	1.2	ug/L
	Se	77	0.024	**49.230**	0.96	1.9	ug/L
	Se	82	0.029	**50.027**	1.18	2.4	ug/L
>	Y	89	99308.137				ug/L
	Mo	95	2.773	**50.914**	0.37	0.7	ug/L
	Mo	97	1.742	**50.914**	0.40	0.8	ug/L
	Mo	98	4.499	**50.919**	0.29	0.6	ug/L
	Ag	107	1.740	**50.022**	1.17	2.3	ug/L
	Ag	109	1.642	**50.020**	1.37	2.7	ug/L
	Cd	106	0.041	**49.734**	0.36	0.7	ug/L
	Cd	108	0.032	**49.648**	0.57	1.1	ug/L
	Cd	111	0.406	**50.035**	0.70	1.4	ug/L

|	Cd	114	0.929	**50.025**	0.29	0.6	ug/L
|>	In	115	399392.313				ug/L
|	Sb	121	1.322	**49.970**	0.60	1.2	ug/L
|	Sb	123	1.021	**50.010**	0.59	1.2	ug/L
|	Ba	135	0.349	**50.009**	0.70	1.4	ug/L
|	Ba	137	0.601	**49.999**	0.54	1.1	ug/L
|	Tl	203	1.876	**49.996**	0.20	0.4	ug/L
|	Tl	205	4.438	**49.971**	0.76	1.5	ug/L
|	Pb	208	6.180	**50.023**	0.39	0.8	ug/L
|>	Bi	209	277097.520				ug/L
|	Na	23	1.114	**49.615**	0.91	1.8	ug/L
|	Mg	24	0.742	**49.974**	0.93	1.9	ug/L
|	K	39	1.829	**49.931**	2.02	4.1	ug/L
|	Ca	44	0.053	**51.568**	3.44	6.7	ug/L
|	Fe	54	0.145	**50.115**	2.94	5.9	ug/L
|>	Sc	45	452038.058				ug/L
	Kr	83	-11.001				ug/L
	Ru	99	38.334				ug/L
	Pd	105	-1216.851				ug/L
	Sn	118	-1522.894				ug/L
	Br	81	1772.937				ug/L

Freedom_0006095_0594

Quantitative Analysis - Summary Report

Sample ID: cal std 4

Sample Date/Time: Friday, May 20, 2011 14:11:48
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 4.1690
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	419418	0.203	419191.962	1.694
	Be	9	101144	0.150	16.833	11.245
	Al	27	999155	1.175	8656.786	0.338
	Sc	45	438203	1.726	441159.124	2.191
	V	51	1759095	2.984	-33725.922	19.231
	Cr	52	1635507	1.159	32767.677	3.966
	Cr	53	613741	1.909	348181.626	7.828
	Mn	55	2955735	1.397	4559.455	0.876
	Co	59	1940690	1.116	81.334	6.188
	Ni	60	428582	1.971	63.000	22.892
	Ni	62	63402	2.418	122.334	6.025
	Cu	63	937505	1.567	273.004	1.597
	Cu	65	446524	1.160	208.669	4.349
	Zn	66	258181	0.676	2007.555	2.195
	Zn	67	54969	1.463	8119.374	18.535
	Zn	68	181464	1.159	1050.394	8.928
>	Ge	72	509307	0.662	506936.298	1.335
	As	75	297270	0.118	-1639.760	18.549
	Se	77	34704	1.514	11511.293	4.487
	Se	82	29565	0.331	60.571	14.181
>	Y	89	126271	1.334	270431.466	0.598
	Mo	95	539571	0.182	53.000	11.477
	Mo	97	336917	0.460	105.667	3.042
	Mo	98	873563	1.086	30.629	11.067
	Ag	107	1367422	0.702	164.668	8.290
	Ag	109	1297113	0.805	158.335	3.807
	Cd	106	29474	1.147	-2157.317	4.008
	Cd	108	21490	1.952	-2316.105	3.298
	Cd	111	320719	0.923	283.644	7.166

Freedom_0006095_0595

Cd	114	730903	0.111	230.623	35.854
> In	115	395994	0.574	399487.744	1.002
Sb	121	1051153	0.609	673.025	16.561
Sb	123	805134	1.092	525.666	14.841
Ba	135	275816	0.541	72.667	12.712
Ba	137	477824	1.641	112.334	17.292
Tl	203	1024862	1.784	417.343	2.400
Tl	205	2461565	1.227	982.053	0.713
Pb	208	3316270	0.954	1504.716	6.243
> Bi	209	275570	0.838	276943.547	0.692
Na	23	1013626	2.450	22459.386	2.393
Mg	24	670878	1.129	1018.724	3.136
K	39	2647598	0.328	1084510.719	0.460
Ca	44	143985	0.541	92085.044	0.662
Fe	54	206192	1.522	75752.787	0.596
> Sc	45	438203	1.726	441159.124	2.191
Kr	83	483	4.347	443.677	3.077
Ru	99	84	12.267	22.000	24.052
Pd	105	969	1.504	1981.883	3.101
Sn	118	461	4.887	2076.911	21.323
Br	81	37667	0.824	36512.847	0.653

Concentration Results

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
> Li	6	419417.827				ug/L
Be	9	0.241	**100.147**	0.33	0.3	ug/L
Al	27	2.362	**100.032**	1.31	1.3	ug/L
Sc	45	-2955.835				ug/L
V	51	3.520	**98.667**	2.68	2.7	ug/L
Cr	52	3.147	**99.707**	0.51	0.5	ug/L
Cr	53	0.518	**95.660**	5.57	5.8	ug/L
Mn	55	5.794	**97.406**	0.96	1.0	ug/L
Co	59	3.810	**99.876**	1.38	1.4	ug/L
Ni	60	0.841	**100.057**	1.51	1.5	ug/L
Ni	62	0.124	**99.954**	1.83	1.8	ug/L
Cu	63	1.840	**100.076**	1.11	1.1	ug/L
Cu	65	0.876	**99.920**	0.76	0.8	ug/L
Zn	66	0.503	**100.206**	0.25	0.2	ug/L
Zn	67	0.092	**98.874**	0.93	0.9	ug/L
Zn	68	0.354	**99.748**	0.54	0.5	ug/L
> Ge	72	509307.303				ug/L
As	75	0.587	**99.978**	0.76	0.8	ug/L
Se	77	0.045	**98.445**	3.16	3.2	ug/L
Se	82	0.058	**99.811**	0.55	0.6	ug/L
> Y	89	126270.656				ug/L
Mo	95	4.273	**94.634**	1.11	1.2	ug/L
Mo	97	2.668	**94.497**	1.69	1.8	ug/L
Mo	98	6.919	**94.590**	1.50	1.6	ug/L
Ag	107	3.453	**99.853**	0.99	1.0	ug/L
Ag	109	3.275	**99.955**	1.00	1.0	ug/L
Cd	106	0.080	**99.358**	0.93	0.9	ug/L
Cd	108	0.060	**98.469**	2.15	2.2	ug/L
Cd	111	0.809	**99.961**	1.29	1.3	ug/L

Freedom_0006095_0596

	Cd	114	1.845	**99.873**	0.56	0.6	ug/L
>	In	115	395994.444				ug/L
	Sb	121	2.653	**100.052**	0.04	0.0	ug/L
	Sb	123	2.032	**99.906**	1.65	1.6	ug/L
	Ba	135	0.696	**99.930**	0.27	0.3	ug/L
	Ba	137	1.206	**100.066**	1.54	1.5	ug/L
	Tl	203	3.718	**99.805**	2.51	2.5	ug/L
	Tl	205	8.930	**100.114**	1.80	1.8	ug/L
	Pb	208	12.029	**99.445**	1.01	1.0	ug/L
>	Bi	209	275570.136				ug/L
	Na	23	2.263	**100.162**	3.45	3.4	ug/L
	Mg	24	1.529	**100.609**	2.85	2.8	ug/L
	K	39	3.585	**99.546**	2.61	2.6	ug/L
	Ca	44	0.120	**103.193**	4.89	4.7	ug/L
	Fe	54	0.299	**100.703**	4.60	4.6	ug/L
>	Sc	45	438203.289				ug/L
	Kr	83	39.669				ug/L
	Ru	99	61.667				ug/L
	Pd	105	-1013.165				ug/L
	Sn	118	-1615.566				ug/L
	Br	81	1153.694				ug/L

Quantitative Analysis - Summary Report

Sample ID: Blank

Sample Date/Time: Friday, May 20, 2011 14:16:24
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\Blank.1691
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	406383	1.217	419191.962	1.694
	Be	9	27	12.963	16.833	11.245
	Al	27	8467	1.847	8656.786	0.338
	Sc	45	430141	1.418	441159.124	2.191
	V	51	-31770	11.025	-33725.922	19.231
	Cr	52	34586	2.246	32767.677	3.966
	Cr	53	393179	1.966	348181.626	7.828
	Mn	55	3654	5.980	4559.455	0.876
	Co	59	264	20.148	81.334	6.188
	Ni	60	89	8.102	63.000	22.892
	Ni	62	119	17.723	122.334	6.025
	Cu	63	375	15.123	273.004	1.597
	Cu	65	240	15.213	208.669	4.349
	Zn	66	1736	1.531	2007.555	2.195
	Zn	67	10873	3.319	8119.374	18.535
	Zn	68	1061	2.460	1050.394	8.928
>	Ge	72	496695	0.370	506936.298	1.335
	As	75	-1070	49.010	-1639.760	18.549
	Se	77	12094	1.655	11511.293	4.487
	Se	82	58	47.244	60.571	14.181
>	Y	89	260319	0.352	270431.466	0.598
	Mo	95	125	19.121	53.000	11.477
	Mo	97	161	7.163	105.667	3.042
	Mo	98	149	33.275	30.629	11.067
	Ag	107	319	27.002	164.668	8.290
	Ag	109	306	17.435	158.335	3.807
	Cd	106	-1997	4.987	-2157.317	4.008
	Cd	108	-2169	5.451	-2316.105	3.298
	Cd	111	253	10.943	283.644	7.166

Freedom_0006095_0598

	Cd	114	138	21.120	230.623	35.854
>	In	115	385109	1.104	399487.744	1.002
	Sb	121	2765	19.091	673.025	16.561
	Sb	123	2150	18.096	525.666	14.841
	Ba	135	87	16.044	72.667	12.712
	Ba	137	147	15.910	112.334	17.292
	Tl	203	428	3.518	417.343	2.400
	Tl	205	1036	13.818	982.053	0.713
	Pb	208	1000	12.992	1504.716	6.243
>	Bi	209	268518	0.350	276943.547	0.692
	Na	23	20516	2.894	22459.386	2.393
	Mg	24	1060	6.725	1018.724	3.136
	K	39	1068330	1.234	1084510.719	0.460
	Ca	44	89569	0.309	92085.044	0.662
	Fe	54	71471	1.602	75752.787	0.596
>	Sc	45	430141	1.418	441159.124	2.191
	Kr	83	442	4.334	443.677	3.077
	Ru	99	19	13.925	22.000	24.052
	Pd	105	1854	5.468	1981.883	3.101
	Sn	118	349	4.611	2076.911	21.323
	Br	81	35546	1.623	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	406382.673				ug/L
	Be	9	0.000	0.011	0.00	35.8	ug/L
	Al	27	0.000	0.008	0.02	311.0	ug/L
	Sc	45	-11017.850				ug/L
	V	51	0.003	0.072	0.20	282.3	ug/L
	Cr	52	0.005	0.158	0.05	32.4	ug/L
	Cr	53	0.105	19.339	3.26	16.9	ug/L
	Mn	55	-0.002	-0.028	0.01	25.3	ug/L
	Co	59	0.000	0.010	0.00	28.3	ug/L
	Ni	60	0.000	0.007	0.00	26.0	ug/L
	Ni	62	-0.000	-0.002	0.03	1659.1	ug/L
	Cu	63	0.000	0.012	0.01	51.4	ug/L
	Cu	65	0.000	0.008	0.01	100.5	ug/L
	Zn	66	-0.000	-0.092	0.01	13.5	ug/L
	Zn	67	0.006	6.322	0.86	13.6	ug/L
	Zn	68	0.000	0.018	0.02	92.6	ug/L
>	Ge	72	496694.776				ug/L
	As	75	0.001	0.185	0.18	96.5	ug/L
	Se	77	0.002	3.557	1.07	30.0	ug/L
	Se	82	-0.000	-0.006	0.09	1689.3	ug/L
>	Y	89	260318.878				ug/L
	Mo	95	0.000	0.006	0.00	32.4	ug/L
	Mo	97	0.000	0.008	0.00	19.5	ug/L
	Mo	98	0.000	0.006	0.00	41.6	ug/L
	Ag	107	0.000	0.012	0.01	54.6	ug/L
	Ag	109	0.000	0.012	0.00	36.3	ug/L
	Cd	106	0.000	0.268	0.27	101.8	ug/L
	Cd	108	0.000	0.273	0.45	163.7	ug/L
	Cd	111	-0.000	-0.007	0.01	138.5	ug/L

All quantifiers <MRL

|	Cd	114	-0.000	**-0.012**	0.00	35.5	ug/L
|>	In	115	385108.717				ug/L
|	Sb	121	0.005	**0.207**	0.05	25.5	ug/L
|	Sb	123	0.004	**0.210**	0.05	24.2	ug/L
|	Ba	135	0.000	**0.006**	0.01	83.3	ug/L
|	Ba	137	0.000	**0.008**	0.01	62.8	ug/L
|	Tl	203	0.000	**0.002**	0.00	63.3	ug/L
|	Tl	205	0.000	**0.004**	0.01	168.7	ug/L
|	Pb	208	-0.002	**-0.014**	0.00	27.7	ug/L
|>	Bi	209	268517.577				ug/L
|	Na	23	-0.003	**-0.142**	0.06	40.0	ug/L
|	Mg	24	0.000	**0.010**	0.01	92.3	ug/L
|	K	39	0.026	**0.718**	1.62	226.3	ug/L
|	Ca	44	-0.000	**-0.404**	2.96	731.5	ug/L
|	Fe	54	-0.006	**-1.872**	0.11	5.7	ug/L
|>	Sc	45	430141.274				ug/L
	Kr	83	-1.667				ug/L
	Ru	99	-3.000				ug/L
	Pd	105	-128.360				ug/L
	Sn	118	-1727.904				ug/L
	Br	81	-966.810				ug/L

Freedom_0006095_0600

Quantitative Analysis - Summary Report

Sample ID: ICV
Sample Date/Time: Friday, May 20, 2011 14:21:01
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\ICV.1692
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	414271	1.963	419191.962	1.694
	Be	9	49849	1.092	16.833	11.245
	Al	27	492285	1.591	8656.786	0.338
	Sc	45	422421	1.058	441159.124	2.191
	V	51	884351	1.287	-33725.922	19.231
	Cr	52	828546	1.243	32767.677	3.966
	Cr	53	497010	1.179	348181.626	7.828
	Mn	55	1624132	2.700	4559.455	0.876
	Co	59	965277	0.669	81.334	6.188
	Ni	60	209830	1.101	63.000	22.892
	Ni	62	31292	0.910	122.334	6.025
	Cu	63	464514	0.893	273.004	1.597
	Cu	65	221866	1.062	208.669	4.349
	Zn	66	127298	0.800	2007.555	2.195
	Zn	67	32149	1.930	8119.374	18.535
	Zn	68	90815	0.518	1050.394	8.928
>	Ge	72	501834	1.236	506936.298	1.335
	As	75	144973	1.268	-1639.760	18.549
	Se	77	23368	1.138	11511.293	4.487
	Se	82	14725	1.140	60.571	14.181
>	Y	89	97477	1.272	270431.466	0.598
	Mo	95	272399	0.550	53.000	11.477
	Mo	97	168632	1.234	105.667	3.042
	Mo	98	432912	0.683	30.629	11.067
	Ag	107	680032	1.806	164.668	8.290
	Ag	109	644984	0.610	158.335	3.807
	Cd	106	14158	1.081	-2157.317	4.008
	Cd	108	10389	2.299	-2316.105	3.298
	Cd	111	157118	0.326	283.644	7.166

Freedom_0006095_0601

	Cd	114	361667	0.224	230.623	35.854
>	In	115	389078	0.486	399487.744	1.002
	Sb	121	527617	0.312	673.025	16.561
	Sb	123	404609	0.675	525.666	14.841
	Ba	135	136818	0.821	72.667	12.712
	Ba	137	236489	1.198	112.334	17.292
	Tl	203	511653	0.470	417.343	2.400
	Tl	205	1211029	0.209	982.053	0.713
	Pb	208	1663543	1.043	1504.716	6.243
>	Bi	209	268670	1.155	276943.547	0.692
	Na	23	511058	2.245	22459.386	2.393
	Mg	24	326850	0.334	1018.724	3.136
	K	39	1878624	0.326	1084510.719	0.460
	Ca	44	115712	0.609	92085.044	0.662
	Fe	54	137235	1.139	75752.787	0.596
>	Sc	45	422421	1.058	441159.124	2.191
	Kr	83	423	1.679	443.677	3.077
	Ru	99	50	15.100	22.000	24.052
	Pd	105	724	3.215	1981.883	3.101
	Sn	118	350	2.983	2076.911	21.323
	Br	81	37167	2.483	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	414271.469				ug/L
	Be	9	0.120	49.972	0.86	1.7	ug/L
	Al	27	1.168	49.471	1.18	2.4	ug/L
	Sc	45	-18738.452				ug/L
	V	51	1.829	51.265	1.16	2.3	ug/L
	Cr	52	1.587	50.280	1.27	2.5	ug/L
	Cr	53	0.304	56.042	3.31	5.9	ug/L
	Mn	55	3.228	54.272	2.15	4.0	ug/L
	Co	59	1.923	50.417	0.53	1.1	ug/L
	Ni	60	0.418	49.720	1.14	2.3	ug/L
	Ni	62	0.062	49.983	1.06	2.1	ug/L
	Cu	63	0.925	50.312	0.22	0.4	ug/L
	Cu	65	0.442	50.370	0.83	1.7	ug/L
	Zn	66	0.250	49.757	1.02	2.0	ug/L
	Zn	67	0.048	51.698	1.80	3.5	ug/L
	Zn	68	0.179	50.380	0.42	0.8	ug/L
>	Ge	72	501833.989				ug/L
	As	75	0.292	49.766	0.96	1.9	ug/L
	Se	77	0.024	51.700	1.65	3.2	ug/L
	Se	82	0.029	50.357	1.21	2.4	ug/L
>	Y	89	97476.864				ug/L
	Mo	95	2.794	61.884	0.52	0.8	ug/L
	Mo	97	1.730	61.257	0.79	1.3	ug/L
	Mo	98	4.441	60.721	0.63	1.0	ug/L
	Ag	107	1.747	50.531	0.68	1.3	ug/L
	Ag	109	1.657	50.581	0.56	1.1	ug/L
	Cd	106	0.042	52.009	0.34	0.7	ug/L
	Cd	108	0.032	53.271	0.84	1.6	ug/L
	Cd	111	0.403	49.796	0.38	0.8	ug/L

Acceptance Limits
45.0 - 55.0 ug/L

All quantifiers passed

Freedom_0006095_0602

	Cd	114	0.929	**50.282**	0.25	0.5	ug/L
>	In	115	389077.622				ug/L
	Sb	121	1.354	**51.083**	0.28	0.6	ug/L
	Sb	123	1.039	**51.064**	0.10	0.2	ug/L
	Ba	135	0.351	**50.437**	0.20	0.4	ug/L
	Ba	137	0.608	**50.393**	0.37	0.7	ug/L
	Tl	203	1.903	**51.085**	0.65	1.3	ug/L
	Tl	205	4.504	**50.500**	0.67	1.3	ug/L
	Pb	208	6.186	**51.143**	0.24	0.5	ug/L
>	Bi	209	268669.612				ug/L
	Na	23	1.159	**51.300**	1.24	2.4	ug/L
	Mg	24	0.772	**50.760**	0.56	1.1	ug/L
	K	39	1.989	**55.245**	1.67	3.0	ug/L
	Ca	44	0.065	**56.131**	3.93	7.0	ug/L
	Fe	54	0.153	**51.608**	2.41	4.7	ug/L
>	Sc	45	422420.672				ug/L
	Kr	83	-21.001				ug/L
	Ru	99	28.000				ug/L
	Pd	105	-1257.521				ug/L
	Sn	118	-1726.904				ug/L
	Br	81	654.005				ug/L

Quantitative Analysis - Summary Report

Sample ID: Blank

Sample Date/Time: Friday, May 20, 2011 14:25:38
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\Blank.1693
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	402027	1.207	419191.962	1.694
	Be	9	23	21.763	16.833	11.245
	Al	27	8290	1.344	8656.786	0.338
	Sc	45	421201	0.742	441159.124	2.191
	V	51	-30588	44.142	-33725.922	19.231
	Cr	52	34339	1.524	32767.677	3.966
	Cr	53	393116	1.232	348181.626	7.828
	Mn	55	3149	1.634	4559.455	0.876
	Co	59	162	15.158	81.334	6.188
	Ni	60	79	5.137	63.000	22.892
	Ni	62	115	9.077	122.334	6.025
	Cu	63	278	14.412	273.004	1.597
	Cu	65	204	14.484	208.669	4.349
	Zn	66	1654	0.674	2007.555	2.195
	Zn	67	10672	2.798	8119.374	18.535
	Zn	68	1033	3.655	1050.394	8.928
>	Ge	72	491825	1.576	506936.298	1.335
	As	75	-997	25.054	-1639.760	18.549
	Se	77	12205	1.638	11511.293	4.487
	Se	82	82	46.364	60.571	14.181
>	Y	89	255419	0.840	270431.466	0.598
	Mo	95	99	12.787	53.000	11.477
	Mo	97	121	9.314	105.667	3.042
	Mo	98	98	24.700	30.629	11.067
	Ag	107	221	17.705	164.668	8.290
	Ag	109	214	22.335	158.335	3.807
	Cd	106	-2005	2.385	-2157.317	4.008
	Cd	108	-2149	2.489	-2316.105	3.298
	Cd	111	214	4.261	283.644	7.166

Freedom_0006095_0604

Cd	114	105	13.137	230.623	35.854
> In	115	381695	0.381	399487.744	1.002
Sb	121	2229	15.185	673.025	16.561
Sb	123	1741	14.144	525.666	14.841
Ba	135	75	12.893	72.667	12.712
Ba	137	118	22.900	112.334	17.292
Tl	203	358	12.500	417.343	2.400
Tl	205	822	6.651	982.053	0.713
Pb	208	794	11.211	1504.716	6.243
> Bi	209	267530	0.391	276943.547	0.692
Na	23	20702	1.698	22459.386	2.393
Mg	24	970	4.962	1018.724	3.136
K	39	1044074	0.917	1084510.719	0.460
Ca	44	88403	0.379	92085.044	0.662
Fe	54	71539	1.090	75752.787	0.596
> Sc	45	421201	0.742	441159.124	2.191
Kr	83	430	6.647	443.677	3.077
Ru	99	21	11.175	22.000	24.052
Pd	105	1836	2.236	1981.883	3.101
Sn	118	272	6.432	2076.911	21.323
Br	81	35200	2.116	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	402026.565				ug/L
	Be	9	0.000	0.007	0.01	78.1	ug/L
	Al	27	-0.000	-0.001	0.01	721.5	ug/L
	Sc	45	-19958.500				ug/L
	V	51	0.004	0.123	0.77	626.5	ug/L
	Cr	52	0.005	0.164	0.04	21.4	ug/L
	Cr	53	0.113	20.772	2.25	10.8	ug/L
	Mn	55	-0.003	-0.044	0.00	7.3	ug/L
	Co	59	0.000	0.004	0.00	31.1	ug/L
	Ni	60	0.000	0.004	0.00	29.6	ug/L
	Ni	62	-0.000	-0.006	0.02	306.3	ug/L
	Cu	63	0.000	0.001	0.00	332.6	ug/L
	Cu	65	0.000	0.000	0.01	1751.4	ug/L
	Zn	66	-0.001	-0.119	0.01	5.5	ug/L
	Zn	67	0.006	6.111	0.29	4.8	ug/L
	Zn	68	0.000	0.008	0.01	189.2	ug/L
>	Ge	72	491824.665				ug/L
	As	75	0.001	0.205	0.09	44.5	ug/L
	Se	77	0.002	4.566	0.48	10.5	ug/L
	Se	82	0.000	0.082	0.14	166.8	ug/L
>	Y	89	255418.923				ug/L
	Mo	95	0.000	0.004	0.00	24.5	ug/L
	Mo	97	0.000	0.003	0.00	49.5	ug/L
	Mo	98	0.000	0.004	0.00	34.0	ug/L
	Ag	107	0.000	0.005	0.00	60.7	ug/L
	Ag	109	0.000	0.005	0.00	75.6	ug/L
	Cd	106	0.000	0.185	0.14	76.7	ug/L
	Cd	108	0.000	0.276	0.22	79.0	ug/L
	Cd	111	-0.000	-0.018	0.00	16.3	ug/L

All quantifiers <MRL

|	Cd	114	-0.000	**-0.016**	0.00	11.6	ug/L
|>	In	115	381695.346				ug/L
|	Sb	121	0.004	**0.157**	0.03	20.9	ug/L
|	Sb	123	0.003	**0.159**	0.03	19.5	ug/L
|	Ba	135	0.000	**0.002**	0.00	162.9	ug/L
|	Ba	137	0.000	**0.002**	0.01	244.5	ug/L
|	Tl	203	-0.000	**-0.005**	0.00	98.0	ug/L
|	Tl	205	-0.000	**-0.005**	0.00	41.7	ug/L
|	Pb	208	-0.002	**-0.020**	0.00	13.2	ug/L
|>	Bi	209	267530.446				ug/L
|	Na	23	-0.002	**-0.078**	0.03	40.9	ug/L
|	Mg	24	-0.000	**-0.000**	0.01	1534.8	ug/L
|	K	39	0.021	**0.573**	1.04	181.3	ug/L
|	Ca	44	0.001	**0.997**	1.76	176.5	ug/L
|	Fe	54	-0.002	**-0.628**	0.63	99.9	ug/L
|>	Sc	45	421200.623				ug/L
	Kr	83	-13.667				ug/L
	Ru	99	-1.333				ug/L
	Pd	105	-146.031				ug/L
	Sn	118	-1805.240				ug/L
	Br	81	-1312.811				ug/L

Freedom_0006095_0606

Quantitative Analysis - Summary Report

Sample ID: QCS

Sample Date/Time: Friday, May 20, 2011 14:30:13
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\QCS.1694
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈>	Li	6	408762	1.990	419191.962	1.694
|	Be	9	48987	1.888	16.833	11.245
⌊	Al	27	485562	1.721	8656.786	0.338
	Sc	45	415367	1.113	441159.124	2.191
⌈	V	51	851717	1.160	-33725.922	19.231
|	Cr	52	800025	0.498	32767.677	3.966
|	Cr	53	496591	1.788	348181.626	7.828
|	Mn	55	1624880	1.437	4559.455	0.876
|	Co	59	977811	0.300	81.334	6.188
|	Ni	60	208305	1.003	63.000	22.892
|	Ni	62	31081	1.635	122.334	6.025
|	Cu	63	458326	0.300	273.004	1.597
|	Cu	65	221463	1.025	208.669	4.349
|	Zn	66	122472	0.363	2007.555	2.195
|	Zn	67	31478	1.275	8119.374	18.535
|	Zn	68	88363	0.355	1050.394	8.928
|>	Ge	72	492415	1.105	506936.298	1.335
|	As	75	145020	2.540	-1639.760	18.549
|	Se	77	23409	0.883	11511.293	4.487
⌊	Se	82	14625	1.960	60.571	14.181
⌈>	Y	89	75849	0.226	270431.466	0.598
|	Mo	95	274044	1.067	53.000	11.477
|	Mo	97	170765	0.077	105.667	3.042
⌊	Mo	98	437884	0.138	30.629	11.067
⌈	Ag	107	684996	1.250	164.668	8.290
|	Ag	109	645162	1.487	158.335	3.807
|	Cd	106	14693	0.814	-2157.317	4.008
|	Cd	108	10617	1.283	-2316.105	3.298
|	Cd	111	160689	2.270	283.644	7.166

Freedom_0006095_0607

Cd	114	362022	1.612	230.623	35.854
> In	115	383060	0.939	399487.744	1.002
Sb	121	521026	0.437	673.025	16.561
Sb	123	399807	0.319	525.666	14.841
Ba	135	135965	0.730	72.667	12.712
Ba	137	235749	1.091	112.334	17.292
Tl	203	516471	0.540	417.343	2.400
Tl	205	1218494	0.769	982.053	0.713
Pb	208	1684628	1.250	1504.716	6.243
> Bi	209	262966	0.740	276943.547	0.692
Na	23	510565	1.872	22459.386	2.393
Mg	24	323916	1.234	1018.724	3.136
K	39	1828002	1.076	1084510.719	0.460
Ca	44	114628	0.444	92085.044	0.662
Fe	54	137838	0.654	75752.787	0.596
> Sc	45	415367	1.113	441159.124	2.191
Kr	83	441	9.174	443.677	3.077
Ru	99	50	17.124	22.000	24.052
Pd	105	549	10.639	1981.883	3.101
Sn	118	281	4.455	2076.911	21.323
Br	81	37357	2.712	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	408761.784				ug/L
	Be	9	0.120	49.761	0.10	0.2	ug/L
	Al	27	1.167	49.447	0.75	1.5	ug/L
	Sc	45	-25792.547				ug/L
	V	51	1.796	50.349	0.89	1.8	ug/L
	Cr	52	1.560	49.439	0.64	1.3	ug/L
	Cr	53	0.322	59.394	5.06	8.5	ug/L
	Mn	55	3.291	55.326	1.07	1.9	ug/L
	Co	59	1.986	52.050	0.73	1.4	ug/L
	Ni	60	0.423	50.299	0.87	1.7	ug/L
	Ni	62	0.063	50.599	1.39	2.7	ug/L
	Cu	63	0.930	50.595	0.68	1.3	ug/L
	Cu	65	0.449	51.241	0.96	1.9	ug/L
	Zn	66	0.245	48.768	0.69	1.4	ug/L
	Zn	67	0.048	51.552	1.63	3.2	ug/L
	Zn	68	0.177	49.952	0.39	0.8	ug/L
>	Ge	72	492415.358				ug/L
	As	75	0.298	50.713	0.72	1.4	ug/L
	Se	77	0.025	53.802	0.90	1.7	ug/L
	Se	82	0.030	50.960	0.44	0.9	ug/L
>	Y	89	75849.442				ug/L
	Mo	95	3.613	80.007	1.01	1.3	ug/L
	Mo	97	2.251	79.719	0.12	0.1	ug/L
	Mo	98	5.773	78.925	0.09	0.1	ug/L
	Ag	107	1.788	51.702	0.39	0.7	ug/L
	Ag	109	1.684	51.387	0.54	1.0	ug/L
	Cd	106	0.044	54.465	0.70	1.3	ug/L
	Cd	108	0.034	54.942	1.01	1.8	ug/L
	Cd	111	0.419	51.727	0.88	1.7	ug/L

Acceptance Limits
45.0 ug/L - 55.0 ug/L
All quantifiers passed.

Freedom_0006095_0608

	Cd	114	0.944	**51.120**	0.46	0.9	ug/L
>	In	115	383060.246				ug/L
	Sb	121	1.359	**51.238**	0.28	0.5	ug/L
	Sb	123	1.042	**51.253**	0.36	0.7	ug/L
	Ba	135	0.355	**50.916**	0.83	1.6	ug/L
	Ba	137	0.615	**51.033**	1.04	2.0	ug/L
	Tl	203	1.963	**52.682**	0.36	0.7	ug/L
	Tl	205	4.630	**51.909**	0.16	0.3	ug/L
	Pb	208	6.401	**52.915**	0.41	0.8	ug/L
>	Bi	209	262965.884				ug/L
	Na	23	1.178	**52.158**	1.12	2.1	ug/L
	Mg	24	0.778	**51.156**	0.16	0.3	ug/L
	K	39	1.943	**53.957**	2.00	3.7	ug/L
	Ca	44	0.067	**57.878**	2.35	4.1	ug/L
	Fe	54	0.160	**53.951**	1.78	3.3	ug/L
>	Sc	45	415366.577				ug/L
	Kr	83	-3.000				ug/L
	Ru	99	27.667				ug/L
	Pd	105	-1432.866				ug/L
	Sn	118	-1796.240				ug/L
	Br	81	844.456				ug/L

Quantitative Analysis - Summary Report

Sample ID: LRB

Sample Date/Time: Friday, May 20, 2011 14:34:50
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\LRB.1695
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	425239	0.751	419191.962	1.694
	Be	9	21	1.386	16.833	11.245
	Al	27	10206	1.046	8656.786	0.338
	Sc	45	430409	0.591	441159.124	2.191
	V	51	-32342	22.368	-33725.922	19.231
	Cr	52	96904	0.989	32767.677	3.966
	Cr	53	418825	2.692	348181.626	7.828
	Mn	55	16361	1.934	4559.455	0.876
	Co	59	284	18.522	81.334	6.188
	Ni	60	497	8.713	63.000	22.892
	Ni	62	176	5.289	122.334	6.025
	Cu	63	669	4.576	273.004	1.597
	Cu	65	397	7.824	208.669	4.349
	Zn	66	1782	1.090	2007.555	2.195
	Zn	67	11234	3.283	8119.374	18.535
	Zn	68	1119	3.976	1050.394	8.928
>	Ge	72	506875	0.780	506936.298	1.335
	As	75	-1372	14.032	-1639.760	18.549
	Se	77	12743	2.216	11511.293	4.487
	Se	82	31	93.072	60.571	14.181
>	Y	89	16662	3.756	270431.466	0.598
	Mo	95	203	11.136	53.000	11.477
	Mo	97	205	8.579	105.667	3.042
	Mo	98	293	6.221	30.629	11.067
	Ag	107	201	22.877	164.668	8.290
	Ag	109	197	17.158	158.335	3.807
	Cd	106	-132	3.445	-2157.317	4.008
	Cd	108	-145	1.482	-2316.105	3.298
	Cd	111	56	7.279	283.644	7.166

Freedom_0006095_0610

Cd	114	92	23.964	230.623	35.854
> In	115	390812	1.201	399487.744	1.002
Sb	121	4022	21.892	673.025	16.561
Sb	123	3147	20.609	525.666	14.841
Ba	135	83	6.879	72.667	12.712
Ba	137	123	13.183	112.334	17.292
Tl	203	282	6.644	417.343	2.400
Tl	205	646	6.530	982.053	0.713
Pb	208	850	7.958	1504.716	6.243
> Bi	209	268543	0.286	276943.547	0.692
Na	23	27139	0.670	22459.386	2.393
Mg	24	2984	3.140	1018.724	3.136
K	39	1062299	0.962	1084510.719	0.460
Ca	44	89342	1.352	92085.044	0.662
Fe	54	115538	0.535	75752.787	0.596
> Sc	45	430409	0.591	441159.124	2.191
Kr	83	424	6.444	443.677	3.077
Ru	99	11	27.063	22.000	24.052
Pd	105	148	1.351	1981.883	3.101
Sn	118	306	4.198	2076.911	21.323
Br	81	27497	0.444	36512.847	0.653

Concentration Results

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
> Li	6	425238.764				ug/L
Be	9	0.000	0.004	0.00	10.8	ug/L
Al	27	0.003	0.142	0.02	12.5	ug/L
Sc	45	-10750.342				ug/L
V	51	0.003	0.076	0.40	535.5	ug/L
Cr	52	0.127	4.010	0.05	1.2	ug/L
Cr	53	0.139	25.743	4.34	16.8	ug/L
Mn	55	0.023	0.391	0.01	2.9	ug/L
Co	59	0.000	0.010	0.00	26.0	ug/L
Ni	60	0.001	0.102	0.01	10.6	ug/L
Ni	62	0.000	0.085	0.02	19.6	ug/L
Cu	63	0.001	0.042	0.00	7.6	ug/L
Cu	65	0.000	0.042	0.01	17.1	ug/L
Zn	66	-0.000	-0.089	0.01	14.0	ug/L
Zn	67	0.006	6.612	0.74	11.3	ug/L
Zn	68	0.000	0.038	0.03	68.1	ug/L
> Ge	72	506875.351				ug/L
As	75	0.001	0.090	0.06	70.9	ug/L
Se	77	0.002	5.270	1.23	23.3	ug/L
Se	82	-0.000	-0.100	0.10	97.4	ug/L
> Y	89	16661.602				ug/L
Mo	95	0.012	0.265	0.02	8.6	ug/L
Mo	97	0.012	0.422	0.02	5.9	ug/L
Mo	98	0.017	0.239	0.01	3.5	ug/L
Ag	107	0.000	0.003	0.00	119.8	ug/L
Ag	109	0.000	0.003	0.00	84.1	ug/L
Cd	106	0.005	6.300	0.01	0.2	ug/L
Cd	108	0.005	8.895	0.00	0.0	ug/L
Cd	111	-0.001	-0.070	0.00	1.8	ug/L

All quantifiers <MRL except Cr

|	Cd	114	-0.000	**-0.019**	0.00	17.4	ug/L
|>	In	115	390811.909				ug/L
|	Sb	121	0.009	**0.325**	0.09	27.6	ug/L
|	Sb	123	0.007	**0.332**	0.09	26.0	ug/L
|	Ba	135	0.000	**0.004**	0.00	57.4	ug/L
|	Ba	137	0.000	**0.003**	0.00	131.0	ug/L
|	Tl	203	-0.000	**-0.012**	0.00	15.7	ug/L
|	Tl	205	-0.001	**-0.013**	0.00	14.1	ug/L
|	Pb	208	-0.002	**-0.019**	0.00	11.5	ug/L
|>	Bi	209	268542.967				ug/L
|	Na	23	0.012	**0.538**	0.03	5.6	ug/L
|	Mg	24	0.005	**0.304**	0.01	4.0	ug/L
|	K	39	0.010	**0.271**	0.30	110.6	ug/L
|	Ca	44	-0.001	**-0.986**	3.26	330.5	ug/L
|	Fe	54	0.097	**32.581**	0.25	0.8	ug/L
|>	Sc	45	430408.781				ug/L
	Kr	83	-20.001				ug/L
	Ru	99	-11.333				ug/L
	Pd	105	-1833.882				ug/L
	Sn	118	-1770.573				ug/L
	Br	81	-9015.657				ug/L

Freedom_0006095_0612

Quantitative Analysis - Summary Report

Sample ID: MRL 1ppb

Sample Date/Time: Friday, May 20, 2011 14:39:27
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.1686
Number of Replicates: 3
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Dual
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\052011b.sam
Method File: C:\Elandata\Method\200.8 methods\drinkingwater200_8_no_sc_is.mth
Dataset File: C:\Elandata\DataSet\Data\MRL 1ppb.1696
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
>	Li	6	427335	0.866	419191.962	1.694
	Be	9	1058	1.271	16.833	11.245
	Al	27	19918	0.930	8656.786	0.338
	Sc	45	434798	2.645	441159.124	2.191
	V	51	-14725	66.926	-33725.922	19.231
	Cr	52	73911	1.249	32767.677	3.966
	Cr	53	424259	2.537	348181.626	7.828
	Mn	55	41019	1.488	4559.455	0.876
	Co	59	20384	1.753	81.334	6.188
	Ni	60	4491	1.703	63.000	22.892
	Ni	62	771	1.948	122.334	6.025
	Cu	63	10011	0.766	273.004	1.597
	Cu	65	4895	1.931	208.669	4.349
	Zn	66	4249	0.321	2007.555	2.195
	Zn	67	11751	4.502	8119.374	18.535
	Zn	68	3010	2.399	1050.394	8.928
>	Ge	72	511433	0.612	506936.298	1.335
	As	75	1719	14.559	-1639.760	18.549
	Se	77	13383	2.600	11511.293	4.487
	Se	82	315	12.147	60.571	14.181
>	Y	89	29167	2.444	270431.466	0.598
	Mo	95	5675	1.882	53.000	11.477
	Mo	97	3585	0.556	105.667	3.042
	Mo	98	8936	0.864	30.629	11.067
	Ag	107	13966	1.710	164.668	8.290
	Ag	109	13389	0.647	158.335	3.807
	Cd	106	74	36.683	-2157.317	4.008
	Cd	108	-19	77.498	-2316.105	3.298
	Cd	111	3280	2.772	283.644	7.166

Freedom_0006095_0613

	Cd	114	7351	0.955	230.623	35.854
>	In	115	391616	0.336	399487.744	1.002
	Sb	121	12864	0.400	673.025	16.561
	Sb	123	9785	2.916	525.666	14.841
	Ba	135	2777	3.182	72.667	12.712
	Ba	137	4967	1.069	112.334	17.292
	Tl	203	10605	1.379	417.343	2.400
	Tl	205	25290	0.342	982.053	0.713
	Pb	208	35545	1.460	1504.716	6.243
>	Bi	209	273961	1.108	276943.547	0.692
	Na	23	33487	1.617	22459.386	2.393
	Mg	24	8264	2.771	1018.724	3.136
	K	39	1079385	0.097	1084510.719	0.460
	Ca	44	89703	0.584	92085.044	0.662
	Fe	54	91396	1.474	75752.787	0.596
>	Sc	45	434798	2.645	441159.124	2.191
	Kr	83	451	4.461	443.677	3.077
	Ru	99	22	15.725	22.000	24.052
	Pd	105	239	4.348	1981.883	3.101
	Sn	118	310	9.636	2076.911	21.323
	Br	81	27219	1.762	36512.847	0.653

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
>	Li	6	427335.169				ug/L
	Be	9	0.002	1.011	0.02	2.2	ug/L
	Al	27	0.026	1.100	0.03	2.3	ug/L
	Sc	45	-6361.066				ug/L
	V	51	0.038	1.056	0.55	51.6	ug/L
	Cr	52	0.080	2.531	0.03	1.3	ug/L
	Cr	53	0.143	26.344	4.10	15.6	ug/L
	Mn	55	0.071	1.197	0.03	2.3	ug/L
	Co	59	0.040	1.041	0.02	2.3	ug/L
	Ni	60	0.009	1.030	0.02	2.0	ug/L
	Ni	62	0.001	1.018	0.03	3.0	ug/L
	Cu	63	0.019	1.035	0.00	0.4	ug/L
	Cu	65	0.009	1.044	0.02	2.3	ug/L
	Zn	66	0.004	0.866	0.02	1.8	ug/L
	Zn	67	0.007	7.489	1.13	15.0	ug/L
	Zn	68	0.004	1.074	0.04	3.7	ug/L
>	Ge	72	511432.731				ug/L
	As	75	0.007	1.124	0.09	7.6	ug/L
	Se	77	0.003	7.497	1.48	19.8	ug/L
	Se	82	0.000	0.854	0.13	15.2	ug/L
>	Y	89	29166.732				ug/L
	Mo	95	0.194	4.305	0.03	0.6	ug/L
	Mo	97	0.123	4.340	0.08	1.9	ug/L
	Mo	98	0.306	4.189	0.14	3.3	ug/L
	Ag	107	0.035	1.019	0.02	2.1	ug/L
	Ag	109	0.034	1.031	0.01	1.0	ug/L
	Cd	106	0.006	6.957	0.09	1.2	ug/L
	Cd	108	0.006	9.425	0.06	0.6	ug/L
	Cd	111	0.008	0.947	0.03	3.3	ug/L

Acceptance Limits
0.50 - 1.50 µg/L
~~All quantifiers passed except Cr~~ GY
Cr MRL 10ppb

Freedom_0006095_0614

	Cd	114	0.018	**0.985**	0.01	1.0	ug/L
>	In	115	391616.017				ug/L
	Sb	121	0.031	**1.175**	0.01	0.6	ug/L
	Sb	123	0.024	**1.164**	0.04	3.4	ug/L
	Ba	135	0.007	**0.992**	0.03	3.2	ug/L
	Ba	137	0.012	**1.029**	0.01	1.3	ug/L
	Tl	203	0.037	**0.999**	0.01	0.5	ug/L
	Tl	205	0.089	**0.995**	0.01	0.8	ug/L
	Pb	208	0.124	**1.028**	0.01	1.4	ug/L
>	Bi	209	273961.396				ug/L
	Na	23	0.026	**1.156**	0.05	4.2	ug/L
	Mg	24	0.017	**1.099**	0.05	4.4	ug/L
	K	39	0.025	**0.703**	1.77	252.4	ug/L
	Ca	44	-0.002	**-1.986**	5.75	289.4	ug/L
	Fe	54	0.039	**13.005**	2.46	18.9	ug/L
>	Sc	45	434798.058				ug/L
	Kr	83	7.667				ug/L
	Ru	99	0.333				ug/L
	Pd	105	-1742.880				ug/L
	Sn	118	-1767.239				ug/L
	Br	81	-9293.484				ug/L

INITIAL DEMONSTRATION OF CAPABILITY
Method Detection Limit – Data Summary

Method	SM 18th ED 3111B	Analyte	Na
SOP Number/Revision	SM 3111B-2006	Date Completed	4/25/11

Instrument Name and Model Number	Varian Spectra AA/400 Plus w/flame unit
Instrument Software (version)	
Reason for Study	Analyst Validation
Source of Calibration Standard (Name/Lot #)	Ultra Scientific/ L00606
Quality Control Sample (Name/Lot #)	Ricca Chemical Co./ 4008793
Date Fortified Reagent Water was Made	04/15/11
Date Sample and Quality Control was Digested	04/19/11
Concentration of Fortified Reagent Water	2.0 mg/L

Replicate	1	2	3	4	5	6	7	Standard Deviation	%RSD	MDL
Analysis Date	4/20/11	4/20/11	4/20/11	4/21/11	4/21/11	4/25/11	4/25/11			
Results	2.02	2.03	2.01	1.98	1.98	1.97	1.98	0.0237	1.19	0.07

Method Detection Limit (MDL) = SD * T
Where,
T = Student's T value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [T = 3.14 for seven replicates].
SD = Standard deviation of the replicate analysis.

Percent Relative Standard Deviation (%RSD) = SD / M * 100
Where,
SD = Standard deviation of the replicate analysis.
M = Mean value of the replicate analysis.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Analyst

5-24-11
HHR Program Manager-Environmental Chemistry

6-17-11
HHR Program Manager-Quality Control Coordinator

Revision 2.0

Varian SpectrAA 300/400 System Report

CJN

OPERATOR CJN
DATE April 21, 2011
BATCH Na

PROGRAM 5 Na 2.00-20.00 PPM

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	INTEGRATION
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	589.6
FLAME	AIR-ACETYLENE
SAMPLE INTRODUCTION	MANUAL
DELAY TIME	4
TIME CONSTANT	0.50
MEASUREMENT TIME (sec)	4.0
REPLICATES	3
BACKGROUND CORRECTION	OFF
AIR FLOW (L/min)	13.5
ACETYLENE FLOW (L/min)	2.00

CONDITIONS FOR Na

WAVELENGTH	SLIT WIDTH	CONC FOR 0.2 ABS	RELATIVE LAMP INTENSITY
nm	nm	mg/L	
589.0	0.5	0.15	100
589.6	0.5	0.3	60
330.3	0.5	80.0	2

FLAME IS COOL, LEAN-BLUE
NV=NOT VALID
RL=REPORTING LIMIT=0.05 PPM
RB=REPEATED BELOW
BURNER TURNED 90 DEGREES
QCS LOT# 4008793/RICCA

METHOD: SM 3111 B
PMV= 220.2
IDL=0.04 PPM 05-14-09
MDL=0.07 PPM 08-08-06 3DAY MEAN
LDR=40.0 PPM 05-09-05

SAMPLE	CONC PPM	%RSD	MEAN ABS	READINGS		
~~BLANK~~ CJN	~~0.00~~		~~-0.111~~	~~0.111~~	~~0.111~~	~~-0.111~~

INITIAL DEMONSTRATION OF CAPABILITY
Unknown Analysis - Data Summary

Method	SM 18th ED 3111B	Analyte	Na
SOP Number/Revision	SM 3111B-2006	Date Completed	05/12/11

Instrument Name and Model Number	Varian Spectra AA/400 Plus w/flame unit
Instrument Software (version)	
Reason for Study	Analyst Validation
Source of Calibration Standards (Name/Lot #)	Ultra Scientific/ L00606
Quality Control Sample (Name/Lot #)	Ricca Chemical Co./ 4008793
Source of Unknown (Name/Lot#)	Inorganic Ventures/ D2-NA03083
Date Unknown was Made	05/10/11
Date Sample and Quality Control was Digested	05/11/11
Date of Analysis	05/12/11

Replicate	Results	True Value	Percent Recovery	Acceptance Limits
Unknown	12.7mg/L	12.5 mg/L	101.6	11.3-13.8

Quality Control Recovery (% REC) = C_s / TV * 100

Where,

C_s = Result from quality control sample.

TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Carolyn Jannell Napier
Analyst

Gregory W Henry 5-24-11
HHR Program Manager-Environmental Chemistry

6-17-11
HHR Program Manager-Quality Control Coordinator

Revision 2.0

Varian SpectrAA 300/400 System Report

OPERATOR CJN
DATE May 12, 2011
BATCH Na

PROGRAM 5 Na 2.00-20.00 PPM

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	INTEGRATION
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	589.6
FLAME	AIR-ACETYLENE
SAMPLE INTRODUCTION	MANUAL
DELAY TIME	4
TIME CONSTANT	0.50
MEASUREMENT TIME (sec)	4.0
REPLICATES	3
BACKGROUND CORRECTION	OFF
AIR FLOW (L/min)	13.5
ACETYLENE FLOW (L/min)	2.00

CONDITIONS FOR Na

WAVELENGTH	SLIT WIDTH	CONC FOR 0.2 ABS	RELATIVE LAMP INTENSITY
nm	nm	mg/L	
589.0	0.5	0.15	100
589.6	0.5	0.3	60
330.3	0.5	80.0	2

FLAME IS COOL, LEAN-BLUE
NV=NOT VALID
RL=REPORTING LIMIT=0.05 PPM
RB=REPEATED BELOW
BURNER TURNED 90 DEGREES
QCS LOT# RICCA 4008793

METHOD: SM 3111 B
PMV=220.2
IDL=0.04 PPM 05-14-09
MDL=0.07 PPM 08-08-06 3DAY MEAN
LDR=40.0 PPM 05-09-05

INITIAL DEMONSTRATION OF CAPABILITY
Precision and Accuracy - Data Summary

Method	SM 18th ED 3111B	Analyte	Na
SOP Number/Revision	SM 3111B-2006	Date Completed	4/25/11

Instrument Name and Model Number	Varian Spectra AA/400 Plus w/flame unit
Instrument Software (version)	
Reason for Study	Analyst Validation
Source of Calibration Standard (Name / Lot #)	Ultra Scientific/ L00606
Quality Control Sample (Name / Lot #)	Ricca Chemical Co./ 4008793
True Value	5.0 mg/L
Date Quality Control Sample was Made	4/21/11
Date Sample and Quality Control was Digested	4/22/11
Date of Analysis	4/25/11

Replicate	Results	Percent Recovery	
#1	5.01	100.2	
#2	5.02	100.4	
#3	5.04	100.8	
#4	5.00	100.0	
	Mean Recovery (100 ± 10%)	100.4	Source of Limit SOP
	%RSD (<5% RSD)	0.34	Source of Limit SOP

Percent Relative Standard Deviation (%RSD) = SD / M * 100
Where,
SD = Standard deviation of the replicate analysis.
M = Mean value of the replicate analysis.

Quality Control Recovery (% REC) = C_s / TV * 100
Where,
C_s = Result from quality control sample.
TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Carolyn Jannah Napier
Analyst

Geoffrey W Young 5-24-11
HHR Program Manager-Environmental Chemistry

6-17-11
HHR Program Manager-Quality Control Coordinator

Revision 2.0

Varian SpectrAA 300/400 System Report

OPERATOR CJN
DATE April 25, 2011
BATCH ~~Mn~~ Na

PROGRAM 5 Na 2.00-20.00 PPM

INSTRUMENT MODE	ABSORBANCE
CALIBRATION MODE	CONCENTRATION
MEASUREMENT MODE	INTEGRATION
LAMP POSITION	2
LAMP CURRENT (mA)	5
SLIT WIDTH (nm)	0.5
SLIT HEIGHT	NORMAL
WAVELENGTH (nm)	589.6
FLAME	AIR-ACETYLENE
SAMPLE INTRODUCTION	MANUAL
DELAY TIME	4
TIME CONSTANT	0.50
MEASUREMENT TIME (sec)	4.0
REPLICATES	3
BACKGROUND CORRECTION	OFF
AIR FLOW (L/min)	13.5
ACETYLENE FLOW (L/min)	2.00

CONDITIONS FOR Na

WAVELENGTH	SLIT WIDTH	CONC FOR 0.2 ABS	RELATIVE LAMP INTENSITY
nm	nm	mg/L	
589.0	0.5	0.15	100
589.6	0.5	0.3	60
330.3	0.5	80.0	2

FLAME IS COOL, LEAN-BLUE
NV=NOT VALID
RL=REPORTING LIMIT=0.05 PPM
RB=REPEATED BELOW
BURNER TURNED 90 DEGREES
QCS LOT# 4008793/RICCA

METHOD: SM 3111 B
PMV= 220.2
IDL=0.04 PPM 05-14-09
MDL=0.07 PPM 08-08-06 3DAY MEAN
LDR=40.0 PPM 05-09-05

SAMPLE	CONC PPM	%RSD	MEAN ABS	READINGS			
BLANK	0.00		-0.117	-0.117	-0.117	-0.118	
BLANK	0.00		0.000	0.000	-0.000	0.000	
STANDARD 1	2.00	0.0	0.023	0.023	0.023	0.023	
STANDARD 2	5.00	0.1	0.056	0.056	0.056	0.056	r = 0.9999
STANDARD 3	10.00	0.3	0.111	0.111	0.111	0.112	
STANDARD 4	15.00	0.4	0.168	0.169	0.168	0.167	
STANDARD 5	20.00	0.0	0.224	0.224	0.224	0.224	
ICP-10.0 PPM	10.09	0.3	0.112	0.113	0.112	0.112	%R = 100.9
QC BLANK	0.01	0.0	0.000	0.000	0.000	0.000	<MRL
QCS-10.0 PPM	10.01	0.2	0.111	0.112	0.111	0.112	%R = 100.1
LRB	0.01	0.0	0.000	0.000	0.000	0.000	<MRL
MRL 2.00 PPM	2.02	0.8	0.023	0.023	0.023	0.023	%R = 101.0
LFB 10.0 PPM	10.37	0.3	0.115	0.116	0.115	0.116	%R = 103.7
MDL6	1.97	0.3	0.023	0.023	0.023	0.023	
MDL7	1.98	0.5	0.023	0.023	0.023	0.023	
ICP-10.0 PPM	10.05	0.2	0.112	0.112	0.112	0.112	%R = 100.5
QC BLANK	-0.01	0.0	-0.000	-0.000	-0.000	-0.000	<MRL
LRB	0.00	99.9	0.000	0.000	0.000	-0.000	<MRL
MRL 2.00 PPM	1.80	0.8	0.021	0.021	0.021	0.021	%R = 90.0
LFB 10.0 PPM	10.24	0.2	0.114	0.114	0.114	0.114	%R = 102.4
PA1	5.01	0.2	0.056	0.057	0.056	0.056	
PA2	5.02	0.5	0.057	0.057	0.056	0.056	
PA3	5.04	0.3	0.057	0.057	0.057	0.057	
PA4	5.00	0.2	0.056	0.056	0.056	0.056	
ICP-10.0 PPM	10.03	0.5	0.112	0.112	0.111	0.111	%R = 100.3
QC BLANK	0.00	0.0	0.000	0.000	0.000	0.000	<MRL

ULTRA SCIENTIFIC
Analytical Solutions

Certificate of Analysis

Rec 4/14/11

ULTRAgrade™ Solution
Sodium ICP Standard
1000 µg/mL

Catalog Number: ICP-011
Lot Number: L00606
Job Number: J00011542
Lot Issue Date: 06/01/2010
Expiration Date: 07/31/2017

Starting Material:	Sodium Nitrate
Starting Material Purity:	99.999%
Starting Material Lot No.:	BH01292
Matrix:	2% nitric acid in low TOC water (< 50 ppb)
Atomic Weight Na:	22.99

COPY

Certified Value: 1002 ± 2 µg/mL

This Certified Reference Material (CRM) was manufactured and verified in accordance with ULTRA's ISO 9001 registered quality system. The analyte concentrations were verified by our ISO 17025 accredited laboratory to be within ± 2.5%, when compared to calibration standards independently prepared using NIST SRM(s). The certified value and uncertainty value for each analyte is determined gravimetrically.

Classical Wet Assay Method: Theoretical, based on gravimetric measurements

Confirmation by Inductively Coupled Plasma Spectroscopy (ICP / ICP-MS) vs. NIST SRM 3152a

ULTRA uses purified acids, 18 megohm double deionized water, calibrated Class A glassware & meticulously cleaned bottles in the manufacturing of ULTRAgrade standards. Balances used in the manufacturing of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001.

Trace Metallic Impurities in Solution Standard in µg/mL:

*	Al	<0.005	ND	*	Ga	<0.005	ND	n	Nb			n	S		
*	Sb	<0.005	ND	n	Ge			n	Os			n	Ta		
*	As	<0.005	ND	n	Au			*	Pd	<0.005	ND	n	Te		
*	Ba	<0.005	ND	n	Hf			*	P	<0.005	ND	n	Tb		
*	Be	<0.005	ND	n	Ho			*	Pt	<0.005	ND	*	Tl	<0.005	ND
*	Bi	<0.005	ND	*	In	<0.005	ND	*	K	<0.005	D	n	Th		
*	B	<0.005	ND	n	Ir			n	Pr			n	Tm		
*	Cd	<0.005	ND	*	Fe	<0.005	ND	n	Re			*	Sn	<0.005	ND
*	Ca	<0.005	ND	*	La	<0.005	ND	n	Rh			*	Ti	<0.005	ND
n	Ce			*	Pb	<0.005	ND	n	Rb			n	W		
n	Cs			*	Li	<0.005	D	n	Ru			n	U		
*	Cr	<0.005	ND	n	Lu			n	Sm			*	V	<0.005	ND
*	Co	<0.005	ND	*	Mg	<0.005	ND	n	Sc			n	Yb		
*	Cu	<0.005	ND	*	Mn	<0.005	ND	*	Se	<0.005	ND	n	Y		
n	Dy			*	Hg	<0.005	ND	*	Si	<0.005	ND	*	Zn	<0.005	ND
*	Er	<0.005	ND	*	Mo	<0.005	ND	*	Ag	<0.005	ND	n	Zr		
*	Eu	<0.005	ND	n	Nd			s	Na						
*	Gd	<0.005	ND	*	Ni	<0.005	ND	*	Sr	<0.005	ND				

* - element checked for
ND - not detected
i - spectral interference
D - detected
n - not checked for
s - solution standard element

Density of Solution (measured at 21.5 ± 0.5°C): 1.024 g/mL

ACCREDITED

ISO 17025:2005 Accredited A2LA Cert. No. 0851-01

ISO 9001:2008 Registered TUV USA, Inc. Cert. No. 09-1009

250 Smith Street, North Kingstown, RI 02852 USA
401-294-9400 Fax: 295-2330
www.ultrasci.com

William J. Leary
Quality Assurance Manager

Rec 11/8/10

RICCA CHEMICAL COMPANY

Arlington, TX 76012
Pocomoke City, MD 21851
Batesville, IN 47006
http://www.riccachemical.com
1-888-GO-RICCA
customerservice@riccachemical.com

Certificate of Analysis

Sodium AA Standard, 1 mL = 1 mg Na (1,000 ppm Na)
NaCl in 3% HCl

Lot Number: 4008793 Product Number: ANA1KH Expiration Date: AUG 2012 Manufacture Date: 8/30/2010

This is a single element solution that was prepared volumetrically to contain the certified value reported. The uncertainty associated with the certified value is the sum of the estimated errors due to the purity of the raw material, the volumetric preparation of the solution, and transpiration of the solution through the container wall.
The final solution concentration is confirmed by AA, ICP, or ICP-MS, and is traceable to NIST Standard Reference Material 3152a.

Contains:

Name	CAS#	Grade
Hydrochloric Acid, HCl	7647-01-0	Trace Metals
Sodium Chloride, NaCl	7647-14-5	High Purity
Water, Deionized, H2O	7732-18-5	ACS, ASTM D 1193 (Type I)

Test Name	Assay Method	Specification	Result
Appearance	Clarity, Color, Odor	Clear, colorless, odorless	Passed Test
Certified Concentration	Based on accurate volumetric preparation	1000 ± 5 ppm Na	1000 ppm Na

Volumetric glassware complies with Class A tolerance requirements of ASTM E 288 and NIST Circular 434; it is calibrated before first use and recalibrated regularly in accordance with ASTM E 542 and NIST Procedure NBSIR 74-461. Balances are calibrated regularly with weights certified traceable to the NIST national mass standard. Thermometers and temperature probes are calibrated before first use and recalibrated regularly with a thermometer traceable to NIST standards. All products are prepared according to master documents that assure manufacture according to validated methods. Batch records document raw material traceability and production and testing history of each lot manufactured.

Shelf Life (unopened container):

Part Number	Shelf Life
ANA1KH-100	24 months
ANA1KH-500	24 months

Recommended Storage: 15°C - 30°C (59°F - 86°F)

LaNelle Ohlhausen
Quality Assurance

COPY

This Certificate of Analysis is designed to comply with ISO Guide 31 "Reference Materials -- Contents of Certificates and Labels."
To determine manufacturing site using lot number, visit www.riccachemical.com/AboutUs/lot.pdf.

Version: 1

INITIAL DEMONSTRATION OF CAPABILITY
Unknown Analysis - Data Summary

Method	EPA 200.8 R 5.4	Analyte	Mercury
SOP Number/Revision	ICPMS2008 R 2	Date Completed	2/27/12

Instrument Name and Model Number	Perkin Elmer Elan 9000
Instrument Software (version)	Elan 3.4
Reason for Study	Demonstration of Capability Study
Source of Calibration Standards (Name/Lot #)	Ultra Scientific L00245
Quality Control Sample (Name/Lot #)	Ricca 4111407
Source of Unknown (Name/Lot#)	ERA WS 187
Date Unknown was Made	2/14/12
Date Sample and Quality Control was Digested	2/24/12
Date of Analysis	2/27/12

Replicate	Results	True Value	Percent Recovery	Acceptance Limits
Unknown	See attachment			

Quality Control Recovery (% REC) = C_S / TV * 100
Where,
C_S = Result from quality control sample.
TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Pat Marchio
Analyst

3-16-12
HHR Program Manager – Environmental Chemistry

3-16-12
HHR Program Manager – Quality Control Coordinator

Revision 2.0

WS-187 2009 TNI Evaluation Final Complete Report

A Waters Company

Gregory Young
DHHR Program Manager I
West Virginia Department of Health
4710 Chimney Dr, Suite G
Environmental Chemistry Lab
Charleston, WV 25302
(304) 965-2694 X 2222

EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/10/12
Study Dates: 02/06/12 - 03/22/12

TNI Analyte Code	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description	Analysis Date	Z Score	Study Mean	Study Standard Deviation	Analyst Name
WS Mercury (cat# 551)												
1095	Mercury	µg/L	6.86	7.60	5.32 - 9.88	Acceptable	EPA 200.8 5.4 1994	2/27/2012	-1.38	7.59	0.531	
WS Mercury (cat# 551)												
1095	Mercury	µg/L	7.26	7.60	5.32 - 9.88	Acceptable	EPA 245.1 3 1994	2/24/2012	-0.628	7.59	0.531	
WS Nitrite (cat# 594)												
1840	Nitrite as N	mg/L	1.71	1.73	1.47 - 1.99	Acceptable	2-013-1-H	2/23/2012	-0.138	1.72	0.0815	
WS Nitrite (cat# 594)												
1840	Nitrite as N	mg/L	1.70	1.73	1.47 - 1.99	Acceptable	EPA 300.0 2.1 1993	2/23/2012	-0.26	1.72	0.0815	
WS o-Phosphate Nutrients (cat# 558)												
1870	ortho-Phosphate as P	mg/L	2.11	1.98	1.68 - 2.28	Acceptable	EPA 300.0 2.1 1993	2/20/2012	1.53	1.98	0.0823	
WS Cyanide (cat# 556)												
1645	Cyanide, total	mg/L	0.134	0.147	0.110 - 0.184	Acceptable	SM4500CN F 18th ED 1992	2/28/2012	-0.95	0.148	0.0152	
WS Organic Carbon (cat# 557)												
1710	Dissolved Organic Carbon (DOC)	mg/L	5.21	6.26	5.55 - 6.89	Not Acceptable	EPA 415.3 1 2003	2/24/2012	-1.48	6.38	0.790	
2040	Total Organic Carbon (TOC)	mg/L		6.26	5.01 - 7.51	Not Reported				6.34	0.383	
WS Turbidity (cat# 592)												
2055	Turbidity	NTU	6.70	7.29	6.21 - 8.13	Acceptable	EPA 180.1 2 1993	2/16/2012	-1.24	7.15	0.362	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0626

INITIAL DEMONSTRATION OF CAPABILITY
Precision and Accuracy - Data Summary

Method	EPA 200.8 R 5.4	Analyte	Mercury
SOP Number/Revision	ICPMS2008 R 2	Date Completed	03/7/12

Instrument Name and Model Number	Perkin Elmer Elan 9000
Instrument Software (version)	Elan 3.4
Reason for Study	Demonstration of Capability Study
Source of Calibration Standard (Name / Lot #)	Ultra Scientific L00245
Quality Control Sample (Name / Lot #)	Ricca 4111407
True Value	5.0 µg/L
Date Quality Control Sample was Made	3/5/12
Date Sample and Quality Control was Digested	3/6/12
Date of Analysis	3/7/12

Replicate	Results	Percent Recovery	
#1	See attachment		
#2			
#3			
#4			
	Mean Recovery (100 ± 10%)	101.3%	Source of Limit SOP
	%RSD (<10% RSD)	0.8%	Source of Limit SOP

Percent Relative Standard Deviation (%RSD) = SD / M * 100
Where,
SD = Standard deviation of the replicate analysis.
M = Mean value of the replicate analysis.

Quality Control Recovery (% REC) = C_S / TV * 100
Where,
C_S = Result from quality control sample.
TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples . have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Pat Marchio
Analyst

Gregory W Young 3-16-12
HHR Program Manager – Environmental Chemistry

8-16-12
HHR Program Manager – Quality Control Coordinator

Revision 2.0

INITIAL DEMONSTRATION OF CAPABILITY
Precision and Accuracy - Data Summary

Analyst: Patrick Marchio
Date of Analysis: 3/7/12
Concentration units: µg/L

Analyte (Mass)	True Value	Replicate 1		Replicate 2		Replicate 3		Replicate 4		Mean Recovery	% RSD	Source of Limits
		Result	Percent Recovery	Result	Percent Recovery	Result	Percent Recovery	Result	Percent Recovery	Limit 100±10%	Limit <10%RSD	
Mercury (202)	5.0	5.021	100.4%	5.035	100.7%	5.091	101.8%	5.108	102.2%	101.3%	0.8%	SOP

GY

Run List

WS-187 Hg 200.8

Sample File Name: 022712.sam

AS Loc.	Sample ID	Batch Index	Sample Type	Method
2	blank		Blank	drinking water hg_200_8.mth
3	cal std 1		Standard	drinking water hg_200_8.mth
4	cal std 2		Standard	drinking water hg_200_8.mth
5	cal std 3		Standard	drinking water hg_200_8.mth
6	cal std 4		Standard	drinking water hg_200_8.mth
7	cal std 5		Standard	drinking water hg_200_8.mth
8	cal std 6		Standard	drinking water hg_200_8.mth
2	Blank	1	Sample	drinking water hg_200_8.mth
7	ICV	2	Sample	drinking water hg_200_8.mth
2	Blank	3	Sample	drinking water hg_200_8.mth
9	QCS	4	Sample	drinking water hg_200_8.mth
10	LRB	5	Sample	drinking water hg_200_8.mth
11	MRL 0.5 ppb	6	Sample	drinking water hg_200_8.mth
12	LFB	7	Sample	drinking water hg_200_8.mth
13	W120222-01	8	Sample	drinking water hg_200_8.mth
14	W120222-01 DDP	9	Sample	drinking water hg_200_8.mth
15	W120222-01 LFM	10	Sample	drinking water hg_200_8.mth
15	W120222-01 LFMD	11	Sample	drinking water hg_200_8.mth
7	CCV	12	Sample	drinking water hg_200_8.mth
2	Blank	13	Sample	drinking water hg_200_8.mth

WS-187

Daily Performance Report

Sample ID: Daily Performance Check
Sample Date/Time: Monday, February 27, 2012 10:47:31
Sample Description:
Method File: C:\Elandata\Method\200.8 Methods\EPA2008 DAILY.mth
Dataset File: C:\Elandata\DataSet\Data\Daily Performance Check.149
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Dual Detector Mode: Dual
Acq. Dead Time(ns): 55
Current Dead Time (ns): 55

Summary

	Analyte	Mass	Meas. Intens. Mean	Net Intens. Mean	Net Intens. SD	Net Intens. RSD
	Be	9.0	9643.5	9643.513	102.476	1.1
	Mg	24.0	102182.3	102182.350	1451.042	1.4
	Co	58.9	230695.1	230695.079	2385.589	1.0
	Rh	102.9	339354.0	339353.976	2000.918	0.6
	In	114.9	411086.9	411086.893	3163.457	0.8
	Pb	208.0	188984.2	188984.241	2742.710	1.5
⌈>	Ba	137.9	315314.5	315314.460	3089.784	1.0
⌊	Ba++	69.0	6180.1	0.020	0.000	0.6
⌈>	Ce	139.9	396235.5	396235.487	3542.812	0.9
⌊	CeO	155.9	9311.0	0.023	0.000	1.8
	Bkgd	220.0	16.2	16.200	1.924	11.9
	Kr	83.9	821.0	821.032	44.505	5.4
	C	12.0	1039267.5	1039267.510	8048.984	0.8

Current Optimization File Data

Current Value	Description
0.87	Nebulizer Gas Flow
5.50	Lens Voltage
1000.00	ICP RF Power
-1550.00	Analog Stage Voltage
750.00	Pulse Stage Voltage
23.00	Discriminator Threshold
-2.00	AC Rod Offset

Current Autolens Data

Analyte	Mass	Num of Pts	DAC Value	Maximum Intensity
Be	9	45	5.8	12591.7
Co	59	45	6.3	239953.5
In	115	45	6.8	422605.6
U	238	45	9.8	415261.5

Freedom_0006095_0630

Calibration Report

Analyte	Mass	Curve Type	Slope	Intercept	Corr Coeff
Hg	201.971	Linear Thru Zero	0.010522	0.000	0.999969
Bi	208.980	Linear Thru Zero	0.000000	0.000	0.000000

Quantitative Analysis - Summary Report

Sample ID: blank

Sample Date/Time: Monday, February 27, 2012 10:59:17
Sample Description:
Solution Type: Blank
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\blank.150
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	25	31.414		
⌊>	Bi	209	259314	1.807		

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202					ug/L
⌊>	Bi	209					ug/L

Freedom_0006095_0632

Quantitative Analysis - Summary Report

Sample ID: cal std 1

Sample Date/Time: Monday, February 27, 2012 11:01:56
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 1.151
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	1330	2.965	25.250	31.414
⌊>	Bi	209	263477	0.764	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.005	**0.500**	0.02	3.6	ug/L
⌊>	Bi	209	263477.235				ug/L

Freedom_0006095_0633

Quantitative Analysis - Summary Report

Sample ID: cal std 2
Sample Date/Time: Monday, February 27, 2012 11:04:35
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 2.152
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	2667	2.014	25.250	31.414
⌊>	Bi	209	263594	1.258	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.010	1.002	0.01	0.8	ug/L
⌊>	Bi	209	263593.817				ug/L

Freedom_0006095_0634

Quantitative Analysis - Summary Report

Sample ID: cal std 3

Sample Date/Time: Monday, February 27, 2012 11:07:15
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 3.153
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
Hg	202	5542	0.794	25.250	31.414
Bi	209	267470	0.752	259314.019	1.807

Concentration Results

Analyte	Mass	Net Intens. Mean	Conc. Mean	Conc. SD	Conc. RSD	Sample Unit
Hg	202	0.021	**2.015**	0.01	0.5	ug/L
Bi	209	267469.822				ug/L

Freedom_0006095_0635

Quantitative Analysis - Summary Report

Sample ID: cal std 4

Sample Date/Time: Monday, February 27, 2012 11:10:05
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 4.154
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	13883	0.581	25.250	31.414
⌊>	Bi	209	268637	0.873	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.052	**5.007**	0.04	0.7	ug/L
⌊>	Bi	209	268637.050				ug/L

Freedom_0006095_0636

Quantitative Analysis - Summary Report

Sample ID: cal std 5
Sample Date/Time: Monday, February 27, 2012 11:12:42
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 5.155
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	28459	0.956	25.250	31.414
⌊>	Bi	209	266729	0.879	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.107	**10.078**	0.06	0.6	ug/L
⌊>	Bi	209	266729.343				ug/L

Freedom_0006095_0637

Quantitative Analysis - Summary Report

Sample ID: cal std 6
Sample Date/Time: Monday, February 27, 2012 11:15:20
Sample Description:
Solution Type: Standard
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\cal std 6.156
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	56527	1.303	25.250	31.414
⌊>	Bi	209	268973	1.481	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.210	**19.966**	0.35	1.8	ug/L
⌊>	Bi	209	268973.181				ug/L

Freedom_0006095_0638

Quantitative Analysis - Summary Report

Sample ID: Blank

Sample Date/Time: Monday, February 27, 2012 11:17:58
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\Blank.157
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	367	7.610	25.250	31.414
⌊>	Bi	209	267745	0.791	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.001	**0.121**	0.01	7.6	ug/L
⌊>	Bi	209	267745.014				ug/L

Freedom_0006095_0639

Quantitative Analysis - Summary Report

Sample ID: ICV

Sample Date/Time: Monday, February 27, 2012 11:20:36
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\ICV.158
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	28611	1.723	25.250	31.414
⌊>	Bi	209	267849	1.870	259314.019	1.807

Limits
9.0 - 11.0 µg/L

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.107	**10.143**	0.09	0.9	ug/L
⌊>	Bi	209	267848.562				ug/L

Freedom_0006095_0640

Quantitative Analysis - Summary Report

Sample ID: Blank

Sample Date/Time: Monday, February 27, 2012 11:23:14
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\Blank.159
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	344	5.444	25.250	31.414
⌊>	Bi	209	266298	2.693	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.001	**0.113**	0.01	7.0	ug/L
⌊>	Bi	209	266297.778				ug/L

<MRL

Freedom_0006095_0641

Quantitative Analysis - Summary Report

Sample ID: QCS

Sample Date/Time: Monday, February 27, 2012 11:25:52
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Ricca
Lot# 4111407

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\QCS.160
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	28645	0.849	25.250	31.414
⌊>	Bi	209	272510	1.523	259314.019	1.807

Concentration Results

Limits ~~90~~ 9.0-11.0 µg/L

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.105	**9.981**	0.07	0.7	ug/L
⌊>	Bi	209	272509.753				ug/L

Freedom_0006095_0642

Quantitative Analysis - Summary Report

Sample ID: LRB

Sample Date/Time: Monday, February 27, 2012 11:28:31
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\LRB.161
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	400	4.276	25.250	31.414
⌊>	Bi	209	272919	1.164	259314.019	1.807

Concentration Results

<MRL

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.001	**0.130**	0.00	3.6	ug/L
⌊>	Bi	209	272919.234				ug/L

Quantitative Analysis - Summary Report

Sample ID: MRL 0.5 ppb

Sample Date/Time: Monday, February 27, 2012 11:31:11
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\MRL 0.5 ppb.162
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	1677	0.953	25.250	31.414
⌊>	Bi	209	280224	1.786	259314.019	1.807

Limits
0.25- 0.75 µg/L

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.006	**0.560**	0.01	2.2	ug/L
⌊>	Bi	209	280223.572				ug/L

Freedom_0006095_0644

Quantitative Analysis - Summary Report

Sample ID: LFB

Sample Date/Time: Monday, February 27, 2012 11:33:51
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\LFB.163
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	6042	1.700	25.250	31.414
⌊>	Bi	209	280624	0.723	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.021	**2.037**	0.04	2.0	ug/L
⌊>	Bi	209	280623.814				ug/L

%R = 101.8

Freedom_0006095_0645

Quantitative Analysis - Summary Report

Sample ID: W120222-01

Sample Date/Time: Monday, February 27, 2012 11:36:31
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\W120222-01.164
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	20222	1.860	25.250	31.414
⌊>	Bi	209	279696	2.224	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.072	**6.863**	0.06	0.9	ug/L
⌊>	Bi	209	279696.495				ug/L

= 6.86 µg/L

Freedom_0006095_0646

Quantitative Analysis - Summary Report

Sample ID: W120222-01 DDP

Sample Date/Time: Monday, February 27, 2012 11:39:10
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\W120222-01 DDP.165
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	19783	1.382	25.250	31.414
⌊>	Bi	209	274062	2.122	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.072	**6.852**	0.10	1.4	ug/L
⌊>	Bi	209	274061.524				ug/L

rpd = 0.16%
$\bar{x}$ = 6.8575

Freedom_0006095_0647

Quantitative Analysis - Summary Report

Sample ID: W120222-01 LFM

Sample Date/Time: Monday, February 27, 2012 11:41:48
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\W120222-01 LFM.166
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	25428	1.363	25.250	31.414
⌊>	Bi	209	274455	1.140	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.093	**8.796**	0.05	0.5	ug/L
⌊>	Bi	209	274455.190				ug/L

%R = 96.6

Freedom_0006095_0648

Quantitative Analysis - Summary Report

Sample ID: W120222-01 LFMD

Sample Date/Time: Monday, February 27, 2012 11:44:26
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\W120222-01 LFMD.167
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	25316	0.792	25.250	31.414
⌊>	Bi	209	273011	0.330	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.093	**8.804**	0.07	0.8	ug/L
⌊>	Bi	209	273011.064				ug/L

rpd = 0.09%
$\bar{x}$ = 8.80

Freedom_0006095_0649

Quantitative Analysis - Summary Report

Sample ID: CCV

Sample Date/Time: Monday, February 27, 2012 11:47:03
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\CCV.168
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	28414	1.051	25.250	31.414
⌊>	Bi	209	270318	1.405	259314.019	1.807

Limits
8.5 - ~~10~~. 11.5 µg/L

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.105	**9.981**	0.04	0.4	ug/L
⌊>	Bi	209	270318.147				ug/L

Freedom_0006095_0650

Quantitative Analysis - Summary Report

Sample ID: Blank

Sample Date/Time: Monday, February 27, 2012 11:49:41
Sample Description:
Solution Type: Sample
Blank File: C:\Elandata\DataSet\Data\blank.150
Number of Replicates: 4
Peak Processing Mode: Average
Signal Profile Processing Mode: Average
Dual Detector Mode: Pulse
Dead Time (ns): 55

Sample File: C:\Elandata\Sample\022712.sam
Method File: C:\Elandata\Method\200.8 methods\drinking water hg_200_8.mth
Dataset File: C:\Elandata\DataSet\Data\Blank.169
Tuning File: C:\Elandata\Tuning\EPA.tun
Optimization File: C:\Elandata\Optimize\EPA.dac
Calibration File:
Calibration Type: External Calibration

Summary

Intensities

	Analyte	Mass	Meas. Intens. Mean	Meas. Intens. RSD	Blank Intensity	Blank Intens. RSD
⌈	Hg	202	452	4.487	25.250	31.414
⌊>	Bi	209	272784	1.521	259314.019	1.807

Concentration Results

	Analyte	Mass	Net Intens. Mean	**Conc. Mean**	Conc. SD	Conc. RSD	Sample Unit
⌈	Hg	202	0.002	**0.148**	0.01	6.2	ug/L
⌊>	Bi	209	272783.532				ug/L

<MRL

Freedom_0006095_0651

ULTRA SCIENTIFIC
Analytical Solutions

Certificate of Analysis

op: 12/13/11

Mercury
AA Standard

Catalog Number: IAA-280
Lot Number: L00245
Job Number: J00011055
Lot Issue Date: 03/10/2010
Expiration Date: 04/30/2017

This Certified Reference Material (CRM) was manufactured and verified in accordance with ULTRA's ISO 9001 registered quality system. The analyte concentrations were verified by our ISO 17025 accredited laboratory to be within ± 2.5%, when compared to calibration standards independently prepared using NIST SRM(s). The certified value and uncertainty value for each analyte is determined gravimetrically.

Analyte	True Value				Analytical Method	NIST SRM
* mercury	1002	±	5	µg/mL	ICP / ICP-MS	3133

Matrix: 2% nitric acid in low TOC water (< 50 ppb)

** light sensitive*

ULTRA uses purified acids, 18 megohm double deionized water, calibrated Class A glassware & meticulously cleaned bottles in the manufacturing of ULTRAgrade standards. Balances used in the manufacturing of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001.

ACCREDITED

ISO 17025:2005
Accredited
A2LA
Cert No 0851.01

ISO 9001:2000
Registered
TUV USA, Inc.
Cert No 06-1004

William J. Leary
Quality Assurance Manager

250 Smith Street, North Kingstown, RI 02852 USA
Ph: 401-294-9400 * Fax: 401-295-2330
www.ultrasci.com

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Pocomoke City, MD 21851
Batesville, IN 47006
http://www.riccachemical.com
1-888-GO-RICCA
customerservice@riccachemical.com

12/13/11

Certificate of Analysis

Mercury AA Standard, 1 mL = 1 mg Hg (1,000 ppm Hg)
HgO in 3% HNO3

Lot Number: 4111407 Product Number: AHG1KN Expiration Date: NOV 2013 Manufacture Date:11/29/2011

The certified value for this product is confirmed in independent testing by a second qualified chemist.
The final solution concentration is confirmed by AA, ICP, or ICP-MS, and is traceable to NIST Standard Reference Material 3133.
This product number replaces 4800 as of 2007.

Contains:

Name	CAS#	Grade
Mercuric Oxide, HgO	21908-53-2	High Purity
Nitric Acid, HNO3	7697-37-2	Trace Metals
Water, Deionized, H2O	7732-18-5	ACS, ASTM D 1193 (Type I)

Test Name	Assay Method	Specification	Result
Appearance	Clarity, Color, Odor	Clear, colorless, odorless	Passed Test
Assay at 20 °C (traceable to NIST SRM 999)	Titrimetric vs. Potassium Thiocyanate (Volhard's Indicator)	1000 ± 5 ppm Hg	1001.9 ppm Hg

Specification	Reference	Method Number
Mercury AA, 1000 ppm in HNO3	EPA	245.1

Volumetric glassware complies with Class A tolerance requirements of ASTM E 288 and NIST Circular 434; it is calibrated before first use and recalibrated regularly in accordance with ASTM E 542 and NIST Procedure NBSIR 74-461. Balances are calibrated regularly with weights certified traceable to the NIST national mass standard. Thermometers and temperature probes are calibrated before first use and recalibrated regularly with a thermometer traceable to NIST standards. All products are prepared according to master documents that assure manufacture according to validated methods. Batch records document raw material traceability and production and testing history for each lot manufactured.

Shelf Life (unopened container):

Part Number	Shelf Life
AHG1KN-100	24 months
AHG1KN-500	24 months

Recommended Storage: 15°C - 30°C (59°F - 86°F)

LaNelle Ohlhausen
Quality Assurance

This Certificate of Analysis is designed to comply with ISO Guide 31 "Reference Materials -- Contents of Certificates and Labels."

To determine manufacture site using lot number, visit http://www.riccachemical.com/Documents/lot.pdf.

Version 2

INITIAL DEMONSTRATION OF CAPABILITY
Method Detection Limit – Data Summary

Method	EPA 200.8 R 5.4	Analyte	Mercury
SOP Number/Revision	ICPMS2008 R 2	Date Completed	3/13/12

Instrument Name and Model Number	Perkin Elmer Elan 9000
Instrument Software (version)	Elan 3.4
Reason for Study	Demonstration of Capability Study
Source of Calibration Standard (Name/Lot #)	Ultra Scientific L00245
Quality Control Sample (Name/Lot #)	Ricca 4111407
Date Fortified Reagent Water was Made	3/5/12
Date Sample and Quality Control was Digested	3/6/12
Concentration of Fortified Reagent Water	0.5 µg/L

Replicate	1	2	3	4	5	6	7	Standard Deviation	MDL
Analysis Date	See attachment								
Results									

Method Detection Limit (MDL) = SD * T

Where,

T = Student's T value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [T = 3.14 for seven replicates].

SD = Standard deviation of the replicate analysis.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Pat Marchio
Analyst

Geoffrey W Young 3-16-12
HHR Program Manager – Environmental Chemistry

8-16-12
HHR Program Manager – Quality Control Coordinator

Revision 2.0

INITIAL DEMONSTRATION OF CAPABILITY
MDL - Data Summary

Analyst: Patrick Marchio

Concentration units: µg/L

Analyte (Mass)	Fortified Reagent Water		REPLICATES							Standard Deviation	Method Detection Limit
	True Value	Date Analyzed	1	2	3	4	5	6	7		
			3/7/2012	3/7/2012	3/9/2012	3/9/2012	3/9/2012	3/13/2012	3/13/2012		
Mercury (202)	0.500		0.576	0.560	0.579	0.571	0.549	0.603	0.590	0.0180	0.0565

2010

Study Num	EPA Lab Cc	NELAC Ana	Analyte Na	Units	Reported \	Final Assig	Lower And Upper	Performance Eval	Method Description
WS163	WV00003	1005	Antimony	µg/L	29.2	39.3	27.5 - 51.1	Acceptable	SM3113B
WS163	WV00003	1010	Arsenic	µg/L	47.3	43.8	30.7 - 56.9	Acceptable	SM3113B
WS163	WV00003	1520	Asbestos	NA				Not Reported	
WS163	WV00003	1015	Barium	µg/L	2150	2040	1730 - 2350	Acceptable	EPA 200.7
WS163	WV00003	1020	Beryllium	µg/L	2.36	2.42	2.06 - 2.78	Acceptable	SM3113B
WS163	WV00003	1030	Cadmium	µg/L	20.8	22.9	18.3 - 27.5	Acceptable	SM3113B
WS163	WV00003	1040	Chromium	µg/L	22.1	22.7	19.3 - 26.1	Acceptable	SM3113B
WS163	WV00003	1055	Copper	µg/L	441	429	386 - 472	Acceptable	SM3111B
WS163	WV00003	1635	Cyanide (Fi	mg/L	0.341	0.378	0.284 - 0.472	Acceptable	SM4500CN F
WS163	WV00003	1645	Cyanide (T	mg/L				Not Reported	
WS163	WV00003	1730	Fluoride	mg/L	4.04	4.01	3.61 - 4.41	Acceptable	EPA 300.0
WS163	WV00003	1730	Fluoride	mg/L	3.76	4.01	3.61 - 4.41	Acceptable	SM4500F- C
WS163	WV00003	1075	Lead	µg/L	18	18	12.6 - 23.4	Acceptable	SM3113B
WS163	WV00003	1095	Mercury	µg/L	6.02	6.46	4.52 - 8.40	Acceptable	EPA 245.1
WS163	WV00003	1105	Nickel	µg/L	114	109	92.6 - 125	Acceptable	SM3113B
WS163	WV00003	1810	Nitrate	mg/L	4.56	4.55	4.10 - 5.00	Acceptable	EPA 300.0
WS163	WV00003	1810	Nitrate	mg/L	3.85	4.55	4.10 - 5.00	Not Acceptable	EPA 353.2
WS163	WV00003	1840	Nitrite	mg/L	1.42	1.42	1.21 - 1.63	Acceptable	EPA 300.0
WS163	WV00003	1840	Nitrite	mg/L	1.42	1.42	1.21 - 1.63	Acceptable	EPA 353.2
WS163	WV00003	1820	Nitrate anc	mg/L	3.85	4.55	4.04 - 5.00	Not Acceptable	EPA 353.2
WS163	WV00003	1140	Selenium	µg/L	20	20.2	16.2 - 24.2	Acceptable	SM3113B
WS163	WV00003	1155	Sodium	µg/L	12.7	13	11.4 - 14.4	Acceptable	SM3111B
WS163	WV00003	1165	Thallium	µg/L				Not Reported	
WS163	WV00003	1535	Bromate	µg/L				Not Reported	
WS163	WV00003	1595	Chlorite	µg/L				Not Reported	
WS163	WV00003	9357	Dibromoac	µg/L				Not Reported	
WS163	WV00003	9360	Dichloroac	µg/L				Not Reported	
WS163	WV00003	9312	Monobron	µg/L				Not Reported	
WS163	WV00003	9336	Monochlor	µg/L				Not Reported	
WS163	WV00003	9642	Trichloroac	µg/L				Not Reported	
WS163	WV00003	4395	Bromodich	µg/L				Not Reported	
WS163	WV00003	4400	Bromoforn	µg/L				Not Reported	
WS163	WV00003	4505	Chloroforn	µg/L				Not Reported	

WS163	WV00003	4575	Dibromoch	µg/L	Not Reported
WS163	WV00003	5160	1,1,1-Trich	µg/L	Not Reported
WS163	WV00003	5165	1,1,2-Trich	µg/L	Not Reported
WS163	WV00003	4640	1,1-Dichlor	µg/L	Not Reported
WS163	WV00003	5155	1,2,4-Trich	µg/L	Not Reported
WS163	WV00003	4610	1,2-Dichlor	µg/L	Not Reported
WS163	WV00003	4635	1,2-Dichlor	µg/L	Not Reported
WS163	WV00003	4655	1,2-Dichlor	µg/L	Not Reported
WS163	WV00003	4620	1,4-Dichlor	µg/L	Not Reported
WS163	WV00003	4375	Benzene	µg/L	Not Reported
WS163	WV00003	4455	Carbon tet	µg/L	Not Reported
WS163	WV00003	4475	Chloroben	µg/L	Not Reported
WS163	WV00003	4645	cis-1,2-Dic	µg/L	Not Reported
WS163	WV00003	4975	Dichlorom	µg/L	Not Reported
WS163	WV00003	4765	Ethylbenze	µg/L	Not Reported
WS163	WV00003	5100	Styrene	µg/L	Not Reported
WS163	WV00003	5115	Tetrachlor	µg/L	Not Reported
WS163	WV00003	5140	Toluene	µg/L	Not Reported
WS163	WV00003	4700	trans-1,2-D	µg/L	Not Reported
WS163	WV00003	5170	Trichloroet	µg/L	Not Reported
WS163	WV00003	5235	Vinyl chlor	µg/L	Not Reported
WS163	WV00003	5260	Xylenes (to	µg/L	Not Reported
WS163	WV00003	4570	1,2-Dibron	µg/L	Not Reported
WS163	WV00003	8650	2,4,5-TP (S	µg/L	Not Reported
WS163	WV00003	8545	2,4-D (as a	µg/L	Not Reported
WS163	WV00003	7005	Alachlor	µg/L	Not Reported
WS163	WV00003	7065	Atrazine	µg/L	Not Reported
WS163	WV00003	5580	Benzo(a)py	µg/L	Not Reported
WS163	WV00003	7205	Carbofuran	µg/L	Not Reported
WS163	WV00003	7250	Chlordane	µg/L	Not Reported
WS163	WV00003	8555	Dalapon	µg/L	Not Reported
WS163	WV00003	6062	Di(2-ethylh	µg/L	Not Reported
WS163	WV00003	6065	Di(2-ethylh	µg/L	Not Reported
WS163	WV00003	8620	Dinoseb	µg/L	Not Reported

2010

Study Num	EPA Lab Cc	NELAC Analyte	Analyte Na	Units	Reported \	Final Assig	Lower And	Performan	Method Description
090210B	WV00003	1005	Antimony	µg/L	34.2	32.9	23.0 - 42.8	Acceptable	EPA 200.8
090210B	WV00003	1010	Arsenic	µg/L	46.1	45.1	31.6 - 58.6	Acceptable	EPA 200.8
090210B	WV00003	1520	Asbestos	NA					Not Reported
090210B	WV00003	1015	Barium	µg/L	1900	1800	1530 - 207	Acceptable	EPA 200.8
090210B	WV00003	1020	Beryllium	µg/L	3.88	3.91	3.32 - 4.50	Acceptable	EPA 200.8
090210B	WV00003	1030	Cadmium	µg/L	16.1	15.8	12.6 - 19.0	Acceptable	EPA 200.8
090210B	WV00003	1040	Chromium	µg/L	22.4	19.8	16.8 - 22.8	Acceptable	EPA 200.8
090210B	WV00003	1055	Copper	µg/L	1160	1100	990 - 1210	Acceptable	EPA 200.8
090210B	WV00003	1635	Cyanide (F	mg/L					Not Reported
090210B	WV00003	1645	Cyanide (T	mg/L					Not Reported
090210B	WV00003	1730	Fluoride	mg/L					Not Reported
090210B	WV00003	1075	Lead	µg/L	32.4	31.3	21.9 - 40.7	Acceptable	EPA 200.8
090210B	WV00003	1095	Mercury	µg/L					Not Reported
090210B	WV00003	1105	Nickel	µg/L	137	132	112 - 152	Acceptable	EPA 200.8
090210B	WV00003	1810	Nitrate	mg/L					Not Reported
090210B	WV00003	1840	Nitrite	mg/L					Not Reported
090210B	WV00003	1820	Nitrate an	mg/L					Not Reported
090210B	WV00003	1140	Selenium	µg/L	70.1	64.4	51.5 - 77.3	Acceptable	EPA 200.8
090210B	WV00003	1155	Sodium	µg/L					Not Reported
090210B	WV00003	1165	Thallium	µg/L	6.35	5.98	4.19 - 7.77	Acceptable	EPA 200.8
090210B	WV00003	1535	Bromate	µg/L					Not Reported
090210B	WV00003	1595	Chlorite	µg/L					Not Reported
090210B	WV00003	9357	Dibromoac	µg/L					Not Reported
090210B	WV00003	9360	Dichloroac	µg/L					Not Reported
090210B	WV00003	9312	Monobron	µg/L					Not Reported
090210B	WV00003	9336	Monochlo	µg/L					Not Reported
090210B	WV00003	9642	Trichloroa	µg/L					Not Reported
090210B	WV00003	4395	Bromodich	µg/L					Not Reported
090210B	WV00003	4400	Bromoforn	µg/L					Not Reported
090210B	WV00003	4505	Chloroforn	µg/L					Not Reported
090210B	WV00003	4575	Dibromoch	µg/L					Not Reported
090210B	WV00003	5160	1,1,1-Trich	µg/L					Not Reported
090210B	WV00003	5165	1,1,2-Trich	µg/L					Not Reported

090210B	WV00003	4640	1,1-Dichlo	µg/L	Not Reported
090210B	WV00003	5155	1,2,4-Trich	µg/L	Not Reported
090210B	WV00003	4610	1,2-Dichlo	µg/L	Not Reported
090210B	WV00003	4635	1,2-Dichlo	µg/L	Not Reported
090210B	WV00003	4655	1,2-Dichlo	µg/L	Not Reported
090210B	WV00003	4620	1,4-Dichlo	µg/L	Not Reported
090210B	WV00003	4375	Benzene	µg/L	Not Reported
090210B	WV00003	4455	Carbon tet	µg/L	Not Reported
090210B	WV00003	4475	Chloroben	µg/L	Not Reported
090210B	WV00003	4645	cis-1,2-Dic	µg/L	Not Reported
090210B	WV00003	4975	Dichlorom	µg/L	Not Reported
090210B	WV00003	4765	Ethylbenze	µg/L	Not Reported
090210B	WV00003	5100	Styrene	µg/L	Not Reported
090210B	WV00003	5115	Tetrachlor	µg/L	Not Reported
090210B	WV00003	5140	Toluene	µg/L	Not Reported
090210B	WV00003	4700	trans-1,2-D	µg/L	Not Reported
090210B	WV00003	5170	Trichloroet	µg/L	Not Reported
090210B	WV00003	5235	Vinyl chlor	µg/L	Not Reported
090210B	WV00003	5260	Xylenes (to	µg/L	Not Reported
090210B	WV00003	4570	1,2-Dibron	µg/L	Not Reported
090210B	WV00003	8650	2,4,5-TP (S	µg/L	Not Reported
090210B	WV00003	8545	2,4-D (as a	µg/L	Not Reported
090210B	WV00003	7005	Alachlor	µg/L	Not Reported
090210B	WV00003	7065	Atrazine	µg/L	Not Reported
090210B	WV00003	5580	Benzo(a)py	µg/L	Not Reported
090210B	WV00003	7205	Carbofuran	µg/L	Not Reported
090210B	WV00003	7250	Chlordane	µg/L	Not Reported
090210B	WV00003	8555	Dalapon	µg/L	Not Reported
090210B	WV00003	6062	Di(2-ethylh	µg/L	Not Reported
090210B	WV00003	6065	Di(2-ethylh	µg/L	Not Reported
090210B	WV00003	8620	Dinoseb	µg/L	Not Reported
090210B	WV00003	9618	Dioxin (2,3	µg/L	Not Reported
090210B	WV00003	9390	Diquat	µg/L	Not Reported
090210B	WV00003	7525	Endothall	µg/L	Not Reported

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2011

Study: WS-175

ERA Customer Number: W213401

Laboratory Name: West Virginia Department of Health

Inorganic Results

Freedom_0006095_0660

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WS-175 Final Complete Report

Gregory Young
Chemist II
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4710 Chimney Dr, Suite G
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Charleston, WV 25302
(304) 965-2694 X 2222

EPA ID:	**WV00003**
ERA Customer Number:	**W213401**
Report Issued:	**04/13/11**
Study Dates:	**02/07/11 - 03/24/11**
Agency ID:	**WV00003**

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WS Hardness (cat# 555)							
1035	Calcium	mg/L	33.6	32.2	28.7 - 36.3	Acceptable	SM3500Ca D
1085	Magnesium	mg/L	13.4	14.1	12.7 - 15.7	Acceptable	SM3111B
0029	Sodium	mg/L	16.4	16.4	14.4 - 18.1	Acceptable	SM3111B
0025	Calcium Hardness as CaCO3	mg/L	83.8	80.4	71.7 - 90.7	Acceptable	SM3500Ca D
1755	Total Hardness as CaCO3	mg/L	141	138	124 - 155	Acceptable	SM2340C
WS Inorganics (cat# 591)							
0027	Alkalinity as CaCO3	mg/L	79.3	79.5	71.6 - 87.5	Acceptable	SM2320B
1575	Chloride	mg/L	33.1	33.9	30.2 - 37.8	Acceptable	EPA 300.0
1610	Conductivity at 25°C	µmhos/cm	529	548	493 - 603	Acceptable	SM2510B
0010	Fluoride	mg/L	2.54	2.74	2.47 - 3.01	Acceptable	EPA 300.0
1820	Nitrate + Nitrite as N	mg/L	5.35	5.37	4.80 - 5.91	Acceptable	EPA 353.2
0009	Nitrate as N	mg/L	5.35	5.37	4.83 - 5.91	Acceptable	EPA 353.2
1125	Potassium	mg/L		20.6	17.8 - 23.8	Not Reported	
0145	Sulfate	mg/L	96.0	99.4	87.3 - 111	Acceptable	EPA 300.0
0024	Total Dissolved Solids at 180°C	mg/L	412	404	259 - 549	Acceptable	SM2540C
WS Inorganics (cat# 591)							
0027	Alkalinity as CaCO3	mg/L		79.5	71.6 - 87.5	Not Reported	
1575	Chloride	mg/L		33.9	30.2 - 37.8	Not Reported	
1610	Conductivity at 25°C	µmhos/cm		548	493 - 603	Not Reported	
0010	Fluoride	mg/L		2.74	2.47 - 3.01	Not Reported	
1820	Nitrate + Nitrite as N	mg/L		5.37	4.80 - 5.91	Not Reported	
0009	Nitrate as N	mg/L	5.30	5.37	4.83 - 5.91	Acceptable	EPA 300.0
1125	Potassium	mg/L		20.6	17.8 - 23.8	Not Reported	
0145	Sulfate	mg/L		99.4	87.3 - 111	Not Reported	
0024	Total Dissolved Solids at 180°C	mg/L		404	259 - 549	Not Reported	
WS pH (cat# 552)							
0026	pH	S.U.	5.46	5.42	5.22 - 5.62	Acceptable	EPA 150.1

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0661

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WS-175 Final Complete Report

Gregory Young
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EPA ID:	**WV00003**
ERA Customer Number:	**W213401**
Report Issued:	**04/13/11**
Study Dates:	**02/07/11 - 03/24/11**
Agency ID:	**WV00003**

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WS Metals (cat# 590)							
1000	Aluminum	µg/L	1940	2010	1730 - 2220	Acceptable	EPA 200.8
0140	Antimony	µg/L	37.7	37.2	26.0 - 48.4	Acceptable	EPA 200.8
0001	Arsenic	µg/L	27.1	28.8	20.2 - 37.4	Acceptable	EPA 200.8
0002	Barium	µg/L	846	845	718 - 972	Acceptable	EPA 200.8
0141	Beryllium	µg/L	8.61	8.84	7.51 - 10.2	Acceptable	EPA 200.8
0226	Boron	µg/L		1770	1540 - 1960	Not Reported	
0003	Cadmium	µg/L	15.6	15.5	12.4 - 18.6	Acceptable	EPA 200.8
0004	Chromium	µg/L	195	191	162 - 220	Acceptable	EPA 200.8
0091	Copper	µg/L	446	451	406 - 496	Acceptable	EPA 200.8
1070	Iron	µg/L		1130	1010 - 1240	Not Reported	
0005	Lead	µg/L	56.2	55.1	38.6 - 71.6	Acceptable	EPA 200.8
0236	Manganese	µg/L		571	514 - 628	Not Reported	
0237	Molybdenum	µg/L		66.4	57.3 - 73.9	Not Reported	
0142	Nickel	µg/L	75.1	75.9	64.5 - 87.3	Acceptable	EPA 200.8
0007	Selenium	µg/L	71.2	74.0	59.2 - 88.8	Acceptable	EPA 200.8
1150	Silver	µg/L	184	181	160 - 200	Acceptable	EPA 200.8
0143	Thallium	µg/L	5.36	5.16	3.61 - 6.71	Acceptable	EPA 200.8
1185	Vanadium	µg/L		546	491 - 601	Not Reported	
0239	Zinc	µg/L	595	604	544 - 664	Acceptable	EPA 200.8
WS Metals (cat# 590)							
1000	Aluminum	µg/L	2110	2010	1730 - 2220	Acceptable	EPA 200.7
0140	Antimony	µg/L		37.2	26.0 - 48.4	Not Reported	
0001	Arsenic	µg/L		28.8	20.2 - 37.4	Not Reported	
0002	Barium	µg/L	889	845	718 - 972	Acceptable	EPA 200.7
0141	Beryllium	µg/L		8.84	7.51 - 10.2	Not Reported	
0226	Boron	µg/L		1770	1540 - 1960	Not Reported	
0003	Cadmium	µg/L		15.5	12.4 - 18.6	Not Reported	
0004	Chromium	µg/L		191	162 - 220	Not Reported	
0091	Copper	µg/L		451	406 - 496	Not Reported	
1070	Iron	µg/L		1130	1010 - 1240	Not Reported	
0005	Lead	µg/L		55.1	38.6 - 71.6	Not Reported	
0236	Manganese	µg/L		571	514 - 628	Not Reported	
0237	Molybdenum	µg/L		66.4	57.3 - 73.9	Not Reported	
0142	Nickel	µg/L		75.9	64.5 - 87.3	Not Reported	
0007	Selenium	µg/L		74.0	59.2 - 88.8	Not Reported	
1150	Silver	µg/L		181	160 - 200	Not Reported	
0143	Thallium	µg/L		5.16	3.61 - 6.71	Not Reported	
1185	Vanadium	µg/L		546	491 - 601	Not Reported	
0239	Zinc	µg/L		604	544 - 664	Not Reported	

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0662

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WS-175 Final Complete Report

Gregory Young
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(304) 965-2694 X 2222

EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/13/11
Study Dates: 02/07/11 - 03/24/11
Agency ID: WV00003

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WS Metals (cat# 590)							
1000	Aluminum	µg/L		2010	1730 - 2220	Not Reported	
0140	Antimony	µg/L	36.6	37.2	26.0 - 48.4	Acceptable	SM3113B
0001	Arsenic	µg/L	26.3	28.8	20.2 - 37.4	Acceptable	SM3113B
0002	Barium	µg/L		845	718 - 972	Not Reported	
0141	Beryllium	µg/L	8.20	8.84	7.51 - 10.2	Acceptable	SM3113B
0226	Boron	µg/L		1770	1540 - 1960	Not Reported	
0003	Cadmium	µg/L	21.8	15.5	12.4 - 18.6	Not Acceptable	SM3113B
0004	Chromium	µg/L	194	191	162 - 220	Acceptable	SM3113B
0091	Copper	µg/L		451	406 - 496	Not Reported	
1070	Iron	µg/L		1130	1010 - 1240	Not Reported	
0005	Lead	µg/L	54.5	55.1	38.6 - 71.6	Acceptable	SM3113B
0236	Manganese	µg/L		571	514 - 628	Not Reported	
0237	Molybdenum	µg/L		66.4	57.3 - 73.9	Not Reported	
0142	Nickel	µg/L	79.0	75.9	64.5 - 87.3	Acceptable	SM3113B
0007	Selenium	µg/L	67.4	74.0	59.2 - 88.8	Acceptable	SM3113B
1150	Silver	µg/L	176	181	160 - 200	Acceptable	SM3113B
0143	Thallium	µg/L		5.16	3.61 - 6.71	Not Reported	
1185	Vanadium	µg/L		546	491 - 601	Not Reported	
0239	Zinc	µg/L		604	544 - 664	Not Reported	

Atypical E

WS Metals (cat# 590)							
1000	Aluminum	µg/L		2010	1730 - 2220	Not Reported	
0140	Antimony	µg/L		37.2	26.0 - 48.4	Not Reported	
0001	Arsenic	µg/L		28.8	20.2 - 37.4	Not Reported	
0002	Barium	µg/L		845	718 - 972	Not Reported	
0141	Beryllium	µg/L		8.84	7.51 - 10.2	Not Reported	
0226	Boron	µg/L		1770	1540 - 1960	Not Reported	
0003	Cadmium	µg/L		15.5	12.4 - 18.6	Not Reported	
0004	Chromium	µg/L		191	162 - 220	Not Reported	
0091	Copper	µg/L	447	451	406 - 496	Acceptable	SM3111B
1070	Iron	µg/L	1230	1130	1010 - 1240	Acceptable	SM3111B
0005	Lead	µg/L		55.1	38.6 - 71.6	Not Reported	
0236	Manganese	µg/L	630	571	514 - 628	Not Acceptable	SM3111B
0237	Molybdenum	µg/L		66.4	57.3 - 73.9	Not Reported	
0142	Nickel	µg/L		75.9	64.5 - 87.3	Not Reported	
0007	Selenium	µg/L		74.0	59.2 - 88.8	Not Reported	
1150	Silver	µg/L		181	160 - 200	Not Reported	
0143	Thallium	µg/L		5.16	3.61 - 6.71	Not Reported	
1185	Vanadium	µg/L		546	491 - 601	Not Reported	
0239	Zinc	µg/L	606	604	544 - 664	Acceptable	SM3111B

not typical E

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0663

ERA
A Waters Company

WS-175 Final Complete Report

Gregory Young
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Charleston, WV 25302
(304) 965-2694 X 2222

EPA ID: WV00003
ERA Customer Number: W213401
Report Issued: 04/13/11
Study Dates: 02/07/11 - 03/24/11
Agency ID: WV00003

Anal. No.	Analyte	Units	Reported Value	Assigned Value	Acceptance Limits	Performance Evaluation	Method Description
WS Mercury (cat# 551)							
0006	Mercury	µg/L	4.92	4.90	3.43 - 6.37	Acceptable	EPA 245.1
WS Nitrite (cat# 594)							
0092	Nitrite as N	mg/L	1.75	1.83	1.56 - 2.10	Acceptable	EPA 300.0
WS Nitrite (cat# 594)							
0092	Nitrite as N	mg/L	1.84	1.83	1.56 - 2.10	Acceptable	EPA 353.2
WS o-Phosphate Nutrients (cat# 558)							
0261	ortho-Phosphate as P	mg/L	4.60	4.55	4.02 - 5.11	Acceptable	EPA 300.0
WS Cyanide (cat# 556)							
0146	Cyanide	mg/L	0.387	0.470	0.352 - 0.588	Acceptable	SM4500CN F
WS Organic Carbon (cat# 557)							
1710	Dissolved Organic Carbon (DOC)	mg/L	1.57	1.77	1.42 - 2.18	Acceptable	EPA 415.3
0263	Total Organic Carbon (TOC)	mg/L		1.77	1.42 - 2.18	Not Reported	
WS Turbidity (cat# 592)							
0023	Turbidity	NTU	4.17	4.45	3.90 - 5.31	Acceptable	EPA 180.1

All analytes are included in ERA's A2LA accreditation. Lab Code: 1539-01

Freedom_0006095_0664

ENTERED

Method Detection Limit
Data Summary

Method 245.1 Analyte Hg

Analyst PLM Intsrument Cetac M6100

True Value of Fortified Reagent Water (FRW)
used 0.2 µg/L

Date.....	Mean of 7 replicates	Standard Deviation	%RSD	MDL
5/21/08	0.17734	0.00193	1.08	0.006
5/29/08	0.16561	0.00199	1.20	0.006
6/2/08	0.15814	0.00201	1.27	0.006

MDL = Standard Deviation X Student t Value (3.14)

MDL = _____ X 3.14 = _____

MDL average from 3 non-consecutive days = 0.006 ppb

Reviewed by [signature] 6-3-08

INITIAL DEMONSTRATION OF CAPABILITY
Unknown Analysis - Data Summary

Method	EPA 245.1	Analyte	Mercury
SOP Number/Revision	Cetac_Hg_245.1 R 1.0	Date Completed	02/24/12

Instrument Name and Model Number	Cetac Mercury Analyzer M-6100
Instrument Software (version)	Cetac QuickTrace Mercury Analyzer Version 1.5.1
Reason for Study	Demonstration of Capability Study
Source of Calibration Standards (Name/Lot #)	Ultra Scientific Lot # L00245
Quality Control Sample (Name/Lot #)	RICCA Lot # 4111407
Source of Unknown (Name/Lot#)	ERA Proficiency Testing Sample WS 072412L
Date Unknown was Made	2/14/12
Date Sample and Quality Control was Digested	2/24/12
Date of Analysis	2/24/12

Replicate	Results	True Value	Percent Recovery	Acceptance Limits
Unknown	7.26 ug/L	7.60 ug/L	95.5%	5.32 – 9.88

Quality Control Recovery (% REC) = C_s / TV * 100
Where,
C_s = Result from quality control sample.
TV = Known value of analyte concentration.

I the undersigned, Certify that:

1) The analyst identified below, using the cited test method (s), which is in use at the facility for the analysis of samples , have met the Initial Demonstration of Capability.
2) The analyst identified on this certification performed the test method (s).
3) A copy of the test method (s) and the laboratory specific Standard Operating Procedures (SOP) are available for all personnel on site.
4) The data associated with the Demonstration of Capability are true, accurate, and complete and self-explanatory. All raw data necessary to reconstruct and validate these analyses have been retained at the facility, and that the associated information is well-organized and available for review by authorized assessors. This includes all Certificates of Analysis associated with the Demonstration of Capability.

Pat Marsh
Analyst

8-13-12
HHR Program Manager – Environmental Chemistry

8-13-12
HHR Program Manager – Quality Control Coordinator

Revision 2.0

CETAC Hg Analysis Report

64

RLW

Analyst: Mercury Analyzer
Worksheet file: C:\Program Files\QuickTrace\Worksheets\022412b.wsz
Date Started: 2/24/2012 2:28:00 PM
Comment: QCS Lot #
Ricca 4111407

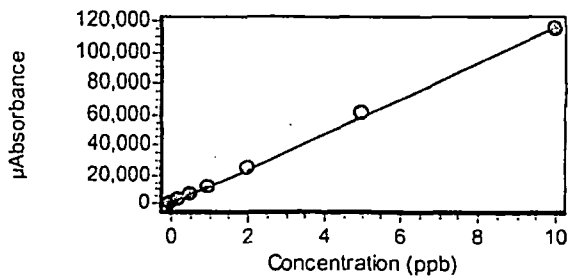
ENTERED

Results

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
Calibration Blank					STD	02/24/12 02:34:12 pm	0.000000	304	4.78	
Replicates	314.3	285.4	316.6	299.3						
0.2 ppb					STD	02/24/12 02:36:57 pm	0.200000	2632	1.28	
Replicates	2659.0	2649.9	2635.9	2583.9						
0.5 ppb					STD	02/24/12 02:39:44 pm	0.500000	6217	0.25	
Replicates	6202.2	6210.5	6238.2	6218.5						
1.0 ppb					STD	02/24/12 02:42:30 pm	1.000000	12118	1.34	
Replicates	11921.1	12049.2	12231.1	12269.1						
2.0 ppb					STD	02/24/12 02:45:18 pm	2.000000	24274	1.06	
Replicates	23898.2	24383.4	24482.3	24331.8						
5.0 ppb					STD	02/24/12 02:48:06 pm	5.000000	60311	0.74	
Replicates	60859.8	60468.5	59871.4	60045.6						
10.0 ppb					STD	02/24/12 02:51:44 pm	10.000000	115182	0.50	
Replicates	115697.8	115515.6	115124.1	114390.1						

Calibration

Equation: A = 744.259 + 11541.630C
R2: 0.99952
SEE: 1009.9720
Flags:



ICV 5.0 ppb					ICV	02/24/12 02:55:42 pm	5.115000	59775	1.59	
Replicates	60968.9	60101.8	59110.9	58916.7						
% Recovery	102.29									

Freedom_0006095_0667

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
ICB					ICB	02/24/12 02:59:28 pm	-0.039100	293	6.68	
Replicates	315.1	301.3	269.7	286.0			<MRL			
Ricca 5.0 ppb LCS					LCS	02/24/12 03:02:17 pm	5.236000	61171	0.12	
Replicates	61079.0	61143.9	61210.4	61249.8						
% Recovery	104.71									
Prep Blank					PBK	02/24/12 03:05:56 pm	-0.034380	347	4.94	
Replicates	349.0	331.6	338.5	370.9			<MRL			
LFB -MRL 0.2 ppb					UNK	02/24/12 03:08:43 pm	0.168000	2684	0.76	
Replicates	2665.0	2668.5	2694.1	2707.5			%R = 84.0			
LFB 2.0 ppb					UNK	02/24/12 03:11:30 pm	1.990000	23710	0.05	
Replicates	23705.2	23702.9	23702.7	23729.4			%R = 99.5			
CCV 5.0 ppb					CCV	02/24/12 03:14:17 pm	5.277000	61651	0.11	
Replicates	61694.1	61677.8	61681.5	61551.6						
% Recovery	105.54									
CCB					CCB	02/24/12 03:17:56 pm	-0.042240	257	2.69	
Replicates	253.4	252.3	254.4	267.1			<MRL			
W120222-01					UNK	02/24/12 03:20:43 pm	7.257000	84501	0.06	
Replicates	84444.0	84539.3	84548.8	84470.4			= 7.26 µg/L			
W120222-01 DUP					DUP	02/24/12 03:24:31 pm	7.278000	84746	0.06	
Replicates	84673.3	84784.3	84768.0	84760.0						
		RPD 0.29								
W120222-01 MSK					MSK	02/24/12 03:28:16 pm	9.194000	106860	0.21	
Replicates	107104.5	106967.9	106762.4	106605.4						
% Recovery	95.80									
W120222-01 MDUP					MSDUP	02/24/12 03:32:06 pm	9.142000	106256	0.07	
Replicates	106141.8	106272.4	106322.0	106289.6						
% Recovery	93.18	RPD 0.57								
W120222-01 2X					UNK	02/24/12 03:36:11 pm	3.691000	43343	0.10	
Replicates	43290.3	43324.2	43373.9	43384.4						

dilution not needed

Freedom_0006095_0668

Sample Name					Type	Date/Time	Conc (ppb)	µAbs	%RSD	Flags
W120222-01 DUP 2X					DUP	02/24/12 03:38:59 pm	3.770000	44255	0.06	
Replicates	44242.6	44229.6	44256.4	44292.6						
		RPD 2.12								
W120222-01 MSK 2X					MSK	02/24/12 03:41:47 pm	4.784000	55957	0.04	N
Replicates	55928.5	55981.4	55961.0	55955.2						
% Recovery	50.69									
W120222-01 MSK 2X					MSK	02/24/12 03:45:25 pm	3.424000	40263	37.04	N
Replicates	54153.0	49350.0	36767.1	20781.0						
% Recovery	-67.99									
W120222-01 MDUP					MSDUP	02/24/12 03:48:12 pm	4.817000	56343	0.07	D
Replicates	56283.3	56362.6	56349.2	56374.9						
% Recovery	1.67	RPD 33.81								
W120222-01 MDUP					MSDUP	02/24/12 03:51:55 pm	3.860000	45295	25.68	D
Replicates	54811.4	52953.9	44092.1	29323.7						
% Recovery	21.80	RPD 22.06								
CCV 5.0 ppb					CCV	02/24/12 03:54:43 pm	5.358000	62586	0.20	
Replicates	62422.1	62550.7	62655.8	62713.6						
% Recovery	107.16									
CCB					ICV	02/24/12 03:58:27 pm	-0.047600	195	18.65	Q
Replicates	224.3	227.4	172.4	155.6						
% Recovery	-0.95						<MRL			
CCB					ICV	02/24/12 04:01:15 pm	-0.041300	268	12.67	Q
Replicates	298.6	292.8	227.8	251.3						
% Recovery	-0.83									

dilution not needed

Notes

MDL (11/17/06) = 0.020 ppb

Linear Dynamic Range (10/27/06) = 35 ppb

LFB and matrix spike concentration = 2.0 ppb

Freedom_0006095_0669

Analysis Parameters

Instrument

Conditions

Gas flow (mL/min)	Sample Uptake (s)	Rinse (s)	Read delay (s)	Replicates (#)	Replicate time (s)	Pump speed (%)	Wavelength (nm)
40	60.00	100.00	61.25	4	3.50		253.65

Instrumental Zero

Zero before first sample: Yes

Zero periodically: Yes

Before each calibration.

Baseline Correction

#1 Start time (s)	#1 End time (s)	#2 Start time (s)	#2 End time (s)
16.50	23.25		

Standby Mode

Enabled: Yes

Standby Options: pump off, gas off, lamp off

Autodilution

Enabled: No

Condition:

Tube # range:

If no autodilution tubes remaining

Calibration

Settings

Algorithm	Through blank	Weighted fit	Cal. Type	Recalibration rate	Reslope rate	Reslope standard
Linear	No	No	Normal	0	0	N/A

Limits

Calibration slope		Reslope		Coeff. of Determination
Lower (%)	Upper (%)	Lower (%)	Upper (%)	
10	180	75	125	0.99500

Error action: Stop analysis

QC

GLP Override: Yes

QC Tests

Freedom_0006095_0670

PBK

Concentration (ppb)
0.0200

Failure flag: Q

Error action for manually inserted QC: Flag and continue

CCB

Concentration (ppb)
0.0200

Failure flag: Q

Error action for manually inserted QC: Flag and continue

ICB

Concentration (ppb)
0.0200

Failure flag: Z

Error action for manually inserted QC: Flag and continue

CCV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

ICV

Concentration (ppb)	Low Limit %	High Limit %
5.0000	95.0000	105.0000

Failure flag: Q

Error action for manually inserted QC: Repeat, flag and continue

LCS

Concentration (ppb)	Low Limit %	High Limit %
5.0000	90.0000	110.0000

Failure flag: L

Error action for manually inserted QC: Repeat, flag and continue

DUP

Concentration (ppb)	Low Limit (ppb)	High Limit (ppb)	RPD
0.2000	0.2000	10.0000	20.0000

Failure flag: D

Error action for manually inserted QC: Flag and continue

Freedom_0006095_0671

Ex. 5 - Deliberative

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