



Department of Energy
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 Carlsbad, New Mexico 88221
DEC 26 2013



Mr. John E. Kieling, Chief
 Hazardous Waste Bureau
 New Mexico Environment Department
 2905 Rodeo Park Drive East, Building 1
 Santa Fe, New Mexico 87505-6303

Subject: Waste Isolation Pilot Plant Contract Laboratory Standard Operating Procedure Updates

Dear Mr. Kieling:

This letter transmits updated Standard Operating Procedures (SOPs) used by the Permittees' contract laboratories for groundwater, volatile organic compound, and hydrogen & methane analyses. These updates were made between December 2012 and November 2013. Enclosed is a CD-ROM that contains updated electronic SOPs.

These revised SOPs are being provided to comply with the Permit Attachment L, Section L-4c(3) and Attachment N, Section N-4e.

We certify under penalty of law that this document and all attachments were prepared under our direction or supervision according to a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on our inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of our knowledge and belief, true, accurate, and complete. We are aware that there are significant penalties for submitting false information, including the possibility of fines and imprisonment for knowing violations.

Please feel free to contact Mr. George T. Basabilvazo at (575) 234-7488 if you have any questions regarding this transmittal.

Sincerely,

Jose R. Franco
 Jose R. Franco, Manager
 Carlsbad Field Office

M. F. Sharif
 M. F. Sharif, Project Manager
 Nuclear Waste Partnership LLC

Enclosure

cc: w/enclosure
 T. Kliphuis, NMED *ED
 *ED denotes electronic distribution



Contract Laboratory Standard Operating Procedures Used for the WIPP Groundwater Detection Monitoring, Volatile Organic Compound Monitoring, and Hydrogen & Methane Monitoring Programs, December 2013

Part 1. Hall Environmental Analysis Laboratory (Groundwater Detection Monitoring Program)

The standard operating procedures (SOPs) for the contract laboratory, Hall Environmental Analysis Laboratory (HEAL), are listed below in the index table. HEAL subcontracts trace metal analysis to Anatek Labs, Inc. The SOP associated with this analysis is also included in the index table. SOPs from HEAL do not itemize the changes within the procedures or highlight these changes; however, the HEAL SOP change summary table summarizes the modifications. Procedures with changes are submitted in compliance with Permit Attachment L, Section L-4c(3).

INDEX TO CONTRACT LABORATORY SOPS – HEAL, 2013

Methods/Analytical Parameters	Current SOP Number	Revised since last submittal to NMED?
SM2710F (specific gravity)	S-SM2710F-2	Yes
SM2320B (alkalinity)	S-SM2320-8	Yes
SM2510B (specific conductance)	S-SM2510B-0	Yes
SM4500-H ⁺ (pH)	S-SM4500-H ⁺ -8	Yes
SM2540D (total suspended solids)	S-SM2540D-5	Yes
SM5310B/EPA Method 9060 (total organic carbon)	S-TOC-6	No
EPA SW-846 Method 8270C (semi-volatiles)	S-8270C-11	No
EPA SW-846 Method 8260B (volatiles)	S-8260-12	Yes
EPA SW-846 Method 6010B (total recoverable metals, dissolved metals)	S-6010-9	Yes
EPA SW-846 Method 7470A (mercury)	S-245.1_7470A-4	Yes
SM2540C (total dissolved solids)	S-SM2540C-8	Yes
EPA Method 300.0 (anions)	S-300.0-11	Yes
EPA SW-846 Method 6020A (trace metal analysis)	ALI-A-315.08	Yes

SM = Standard Methods for the Examination of Water and Wastewater
 EPA = U.S. Environmental Protection Agency

HEAL SOP Change Summary, 2013

Method	Current SOP Number	Effective Date	Supersedes	Summary of Changes*
SM2710F	S-SM2710F-2	5/6/2013	S-SM2710F-1	Updated section 11.1 and appendix B to remove the bench sheet from the SOP and reference its location in the controlled document logbook. Moved the corrective action procedures summary from appendix C to appendix B.
SM2320B	S-SM2320-8	6/10/2013	S-SM2320-7	Removed the comparison study and the instrument setting from the appendices. Removed instrument names throughout the SOP. Made minor changes to the definitions section. Added particulate material to the interferences section. Reorganized sections 7 and 8. Reorganized and reworded sections 10 through 12. Updated section 14 to state that only a practical quantitation limit study and not a method detection limit study is required for the manual procedure. Removed the requirement to set control chart limits for laboratory control samples from section 14 and 18. Updated title page and references to clarify that the method of reference is the 20th edition.
SM2510B	S-SM2510B-0	3/4/2013	S-120.1-7	The reference method was updated from EPA 120.1 to SM2510B. The method summaries from the instrument and the bench sheet have been removed from the SOP and incorporated into the control document logbook.
SM4500-H ⁺	S-SM4500-H ⁺ -8	6/12/2013	S-SM4500-H ⁺ -7	Removed the instrument settings from the appendices and reference there location in the LIMS. Removed instrument names. Updated the instrument materials and reagents and standards sections. Reorganized the SOP and made grammatical changes throughout. Updated the references.

Method	Current SOP Number	Effective Date	Supersedes	Summary of Changes*
SM2540D	S-SM2540D-5	7/1/2013	S-SM2540D-4	Corrected section 7.3 to state that ovens are calibrated quarterly. Added section 8.2 to include the procedure for updating the LCS concentration in the LIMS for new standards. Redefined a sample batch from 10 to 20 samples, still requiring a DUP every 10 samples. Clarified the corrective action required for a DUP failure in 17.2.1. Removed the appendix A bench sheet from the SOP and detailed its location in the LIMS. Several other small clarifications and grammatical corrections throughout the SOP.
EPA SW-846 Method 8260B	S-8260-12	8/30/2013	S-8260-11	Several grammatical changes throughout the document. The instrument specific details in section 6.0 and 8.0 were removed and a reference to their location in the instrument maintenance logbooks was added. Removed detailed concentrations of surrogate and internal standard mixes and added a reference to the logbooks in section 9.2.1. Updated section 9.4 to allow a second source from the same vendor as the primary source so long as they are a verified second source. Added the note in section 9.10.1.1 for chloroform interferences. Restricted the maximum allowable dilution on the Archon to match that of the Atomx. Additional guidance for handling blank failures has been added to 12.2.6.1.
EPA SW-846 Method 6010B	S-6010-9	6/26/2013	S-6010-8	Added a practical quantitation limit check standard to the procedure. Added a definition of post spike to section 4. Updated throughout to include the new 8300DV ICP instrument. Updated section 8 to list data in tables to make it more usable. Changed the procedure from utilizing class A syringes to using calibrated variable volume pipettes when making standards.

Method	Current SOP Number	Effective Date	Supersedes	Summary of Changes*
				Added the formulas for Silica and dry weight reporting. Added the requirement for a linear dynamic range study every 6 months to section 14. Section 17.3 was updated to require different corrective action procedures for MS/MSD failures. Many grammatical changes throughout the document.
EPA SW-846 Method 7470A	S-245.1_7470A-4	1/24/2013	S-245.1_7470A-3	Added section 2.2 to define the specific deviations from the referenced methods. Noted in section 3.1 that method detection limit values can be observed in the LIMS. Added method blank and laboratory control spike to the definitions. Added a couple of supplies to section 7.0 and 8.0. Several grammatical corrections and technical clarifications throughout the document. Added requirements to section 8.11 for supply documentation and the required summary sheet on file in the controlled document logbook. Clarified in section 9.1 that chemical preservation is to a pH <2. Added the requirement and frequency for a laboratory control spike duplicate to sections 10.3.1.1, 16.4.3.4 and 17.3.2. Corrected the block temperature settings in section 12.1 for the new temperature monitoring requirements. Changed the digestion temperature range from 95 ± 5°C to 95 ± 3°C in section 12.1.13. Added significant detail/clarification to the instrument procedure in section 12.3.
SM2540C	S-SM2540C-8	3/21/2013	S-SM2540C-6 and S-SM2540C-7	<u>S-SM2540C-6 to S-SM2540C-7</u> Corrected section 7.3 to state that ovens are calibrated quarterly. Added 150mL glass beakers to section 7. Added section 11.2 to clarify the procedure for checking and replacing the desiccant.

Method	Current SOP Number	Effective Date	Supersedes	Summary of Changes*
				<p>Removed the Appendix A Bench Sheet from the SOP and detailed its presence in the Controlled Document Logbook. Changed the Corrective Action Procedures summary from Appendix B to Appendix A. Updated section 19 to include the 21st edition of Standard methods in the References.</p> <p><u>S-SM2540C-7 to S-SM2540C-8</u> The reference section was updated to include Standard Method for the Examination of Water and Wastewater, 22nd Edition.</p>
EPA Method 300.0	S-300.0-11	1/31/2013	S-300.0-10	Updated supply information in sections 7 and 8. Removed the procedure and specifications for the AS-50 auto sampler throughout the SOP. Numerous changes to the appendices.
EPA SW-846 Method 6020A	ALI-A-315.08	10/7/2013	ALI-A-315.06 and ALI-A-315.07	<p><u>ALI-A-315.06 to ALI-A-315.07</u></p> <ul style="list-style-type: none"> Added preparation details of second Initial Calibration Verification (ICV) solution (ICV1 at 1.0 ppb, ICV2 at 40 ppb). Revision ALI-A-315.06 only listed one ICV at 40 ppb. Clarified acceptance criteria for new ICV levels (ICV1 at 30%, ICV2 at 10%). Revision ALI-A-315.06 only listed one ICV at 10%. <p><u>ALI-A-315.07 to ALI-A-315.08</u></p> <ul style="list-style-type: none"> Updated Equipment and Supplies to reflect new Agilent ICP/MS instrument (Model 7500 to Model 7700) Updated the Pulse Analog Tuning Solution (P/A Factor Solution) text to reflect current practice

Method	Current SOP Number	Effective Date	Supersedes	Summary of Changes*
				<ul style="list-style-type: none"> • Added soil Laboratory Fortified Blank (LFB) MS/MSD spike procedure (not applicable to WIPP Detection Monitoring Program (DMP) groundwater samples) • Updated MS/MSD text – increased frequency to match current practice, added spiking levels for different final volumes, added post-digestion spike and dilution test text from method. • Updated LCS recovery objective from 85 – 115 percent recovery to 80 – 120 percent recovery • Updated TCLP dilution from 10x to 50x to reflect current practice (not applicable to WIPP DMP groundwater samples) • Added EPA Method 1312, Synthetic Precipitation Leaching Procedure, to references (not applicable to WIPP DMP groundwater samples)

SM = Standard Methods for the Examination of Water and Wastewater

EPA = U.S. Environmental Protection Agency

* All SOPs are being distributed with permission from the laboratories

**Contract Laboratory Standard Operating Procedures Used for the WIPP Groundwater
Detection Monitoring, Volatile Organic Compound Monitoring, and Hydrogen & Methane
Monitoring Programs, December 2013**

(Continued)

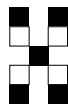
**Part 2. Carlsbad Environmental Monitoring & Research Center (Volatile Organic
Compound and Hydrogen and Methane Monitoring Programs)**

The SOPs and Quality Assurance Project Plan used by Carlsbad Environmental Monitoring & Research Center (CEMRC) to provide contract analytical laboratory services are listed below in the following table. Procedures with changes are submitted in compliance with Permit Attachment N, Section N-4e. Changes are noted on the procedures in the Temporary Procedural Deviation Form, Revision History, and are highlighted.

INDEX TO CONTRACT LABORATORY SOPS – CEMRC, 2013

Procedure Number	Current Revision	Effective Date	Temp Devs	Changed since last submittal to NMED?
OC-PLAN-001-004-020106	4	March 13, 2012	1	No
OC-PROC-002-006-021506	6	September 6, 2013	0	Yes, new revision
OC-PROC-003-004-021706	4	December 12, 2011	2	Yes, +1 temp dev
OC-PROC-004-005-021606	5	February 21, 2012	5	Yes, +1 temp dev
OC-PROC-005-006-022106	6	February 21, 2012	4	Yes, +2 temp devs
OC-PROC-006-004-022006	4	February 21, 2012	0	No
OC-PROC-009-003-110907	3	September 6, 2013	0	Yes, new revision

temp dev = temporary procedural deviation



Hall Environmental Analysis Laboratory

Common Name: Specific Gravity	S.O.P. Number: S-SM2710F-2
Method: SM2710F - Specific Gravity.	
Effective Date: May 6 th , 2013	Supersedes: S-SM2710F-1
Laboratory Manager:	Quality Assurance/Quality Control Officer:

1. Scope and Application

1.1. This SOP is applicable to aqueous samples.

2. Summary of Method

2.1. Remove samples from the refrigerator and allow them to come to room temperature. Add 10mLs sample to a dry, tared 10mL volumetric flask, and record the mass of sample. Calculate the specific gravity using the mass of 10mL of sample and the mass of DI water at 3-5°C. Specific gravity is a unit less measurement.

3. Detection Limits

3.1. PQL/MDL is not applicable to specific gravity.

4. Definitions

4.1. Sample Duplicate (DUP) – Duplicate analysis of sample.

5. Interferences

5.1. Only samples that are aqueous in nature can be analyzed.

6. Safety

6.1. For handling procedures and exposure information always refer to the MSDS. To keep exposure to reagents and standards to a minimum, analysts must wear appropriate laboratory safety attire (i.e. safety glasses, lab coat, and gloves) when working in the laboratory.

7. Apparatus and Materials

7.1. DRY! - 10ml Class A Volumetric Flasks with caps.

7.2. Analytical Balance

7.3. Disposable transfer pipettes.

8. Reagents

8.1. DI water at 3-5°C.

9. Sample Collection, Preservation, and Storage

9.1. Samples are unpreserved and do not require refrigeration. Standard HEAL protocol is to store samples at above freezing to 6°C.

9.2. Currently there is no holding time for specific gravity.

10. Quality Control

10.1. Batch QC

10.1.1. A DUP sample is required in every batch. A batch cannot exceed 20 samples.

11. Procedure

11.1. Use “Specific Gravity Bench Sheet” to document all temperatures, HEAL numbers, and masses. The bench sheet is available through the LIMS and is tracked in the controlled document logbook.

11.2. Remove samples from the refrigerator and allow them to come to room temperature (leave out overnight, so long as this will not interfere with preservation requirements for other tests).

11.3. It is important that the 10mL volumetric flasks and caps are dry. Dry the volumetric flasks and caps overnight in the desiccators if necessary. Use a fresh dry volumetric flask for each sample.

11.4. Label each of the 10mL volumetric flasks with the appropriate sample ID or QC identifier.

11.5. Record room temperature on the bench sheet.

11.6. Weigh and record the tare weight of each of the volumetric flasks and caps. Be sure to include the mass of the cap in the volumetric flask weight. (Keep flask and cap together).

11.7. Remove DI water from the refrigerator (it should be within between 3-5°C). An identical volume bottle shall be stored with the DI water and shall contain a certified thermometer. Record the temperature of the DI water on the Bench Sheet. Using a transfer pipet fill a volumetric flask with DI from the refrigerator to the 10mL mark.

11.8. Cap and record weight.

11.9. For samples use a fresh transfer pipette, fill clean dry volumetric flask to the 10mL mark with sample.

11.10. Cap and record weight.

11.11. Be sure to use a fresh transfer pipette for each sample.

12. Calculations of specific gravity.

$$SG_{T/4^{\circ}C} = \frac{S - W}{R - W} \times F$$

Where:

S = Weight of sample and volumetric flask/cap

W = Weight of empty volumetric flask and cap

R = Weight of water at 4°C

F = Temperature correction factor at room temperature from Table in **Appendix A**.

(Round to the nearest 5°C)

13. Method Performance

13.1. PT or “blind study” samples are not analyzed at this time.

13.2. Estimation of Uncertainty

13.2.1. Estimation of uncertainty is not performed at this time.

13.3. Demonstration of Capability (DOC)

13.3.1. This test is not conducive to DOC. An analyst is deemed capable of performing the specific gravity test on their own after this SOP has been fully read, understood, signed, and dated and has performed the test for the first time under the supervision of the senior analyst who is training them.

14. Pollution Prevention

14.1. Test only uses 10mL of sample, thus only a small amount of sample waste is generated.

15. Data Assessment and Acceptance criteria for Quality Control Measures

15.1. See **Appendix B** for a summary of the quality control measures.

15.2. Batch QC

15.2.1. RPD for DUP sample must be ≤ 20 .

16. Corrective Actions for Out of Control Data

16.1. Batch QC

16.1.1. If sample DUP is unacceptable, reweigh sample. If DUP continues to fail re-prepare sample and DUP.

17. Contingencies for Handling Out of Control Data

17.1. All out of control data is flagged, a corrective action generated, and results reported to the client.

18. Waste Management

18.1. After analysis all samples are disposed of in accordance with the HEAL Chemical Hygiene Plan.

19. References

19.1. Standard Methods for the Examination of Water and Wastewater 20th Edition. 1999, Method 2710F.

19.2. Current revision of HEAL Chemical Hygiene Plan.

Effective Date: May 6th, 2013

SOP Number: S-SM2710F-2

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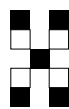
Appendix A

Temperature Correction Factors for Specific Gravity Determination

Temp (°C)	Temperature Correction Factors
15	0.9991
20	0.9982
25	0.9975
30	0.9957
35	0.9941
40	0.9922
45	0.9903

Appendix B
SM2710F - Specific Gravity
Corrective Action Procedures

Analytical Method	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SM2710F Specific Gravity	Met Chemistry	Duplicate (DUP)	1 per preparation/analysis batch (≤ 20 samples)	Relative percent difference (RPD) ≤ 20%	1. Reprep and reanalyze sample and DUP 2. Fill out corrective action and report.



Hall Environmental Analysis Laboratory

Common Name: Standard Methods 2320B, 20 th Edition	S.O.P. Number: S-SM2320-8
Method: Automated and Manual Methods for Total Alkalinity, Low Level Alkalinity, Carbonate, Bicarbonate, and Hydroxide in Aqueous Samples. Including Total CO ₂ calculation.	
Effective Date: June 10, 2013	Supersedes: S-SM2320-7
Laboratory Manager	Quality Assurance/Quality Control Officer:

1.0 Scope and Application

- 1.1. This SOP describes the procedure for determining the total alkalinity and its three common forms found in most waters (carbonate, bicarbonate, and hydroxide). This SOP is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
- 1.2. There are two processes that can be used for alkalinity determination.
 - 1.2.1 Titration of alkalinity by the automated system, Poseidon.
 - 1.2.1.1 The automated titration system is the preferred procedure for the determination of alkalinity. Before use of the automated system, the analyst must have read and understood this SOP and the current pH and eC SOPs within proven demonstration of capability.
 - 1.2.1.1.1 This SOP relies heavily on information already included in the current pH SOP. Any change in the current pH SOP must be adhered to when using this SOP.
 - 1.2.2 Manual titration using a 50mL and or 10mL micro-burette, and a pH meter.
 - 1.2.2.1 The manual titration system is used as a back up system should the auto-titrator system be temporarily out of service, or if analyzing samples that have a difficult matrix with an extreme buffering capacity.
- 1.3. This SOP also includes the procedure for determining low level alkalinities (alkalinities that are less than 20mg/L).
- 1.4. This SOP can be used to calculate Total CO₂ mg/L based on the obtained alkalinity values.

2.0 Summary of method

- 2.1. A 50mL aliquot of sample is titrated with 0.02N H₂SO₄ to the pH 8.3 endpoint (if possible) and the pH 4.5 endpoint. Carbonates, bicarbonates, and hydroxides are calculated from the titration volumes to both the pH 8.3 and 4.5 endpoints.
 - 2.1.1 The automated system (Poseidon) titrates to all pH endpoints and calculates all results.
 - 2.1.1.1 All method parameters and calculations used by the Tiamo software are linked as a PDF under the instrument in the LIMS.
- 2.2. For low level alkalinities 50mL of sample is titrated with 0.02N H₂SO₄ using a 10mL micro burette to pH 4.5 ±0.20 endpoint. Additional titrant is added to lower the pH an additional 0.3 pH units. Low level alkalinity is then calculated from the titration volumes to pH 4.5 and 0.3 pH unit's lower endpoints.
 - 2.2.1 The automated system titrates each sample to a final endpoint of 4.2pH units.
 - 2.2.2 The automated system calculates the low level alkalinity result.

3.0 Detection Limits

- 3.1. The PQL for total alkalinity and bicarbonate is 20 mg/L as CaCO₃. The PQL for carbonate and hydroxide is 2.0 mg/L as CaCO₃.
- 3.2. The PQL for low level alkalinity is 2.0 mg/L as CaCO₃.
- 3.3. MDLs shall be empirically established annually and are subject to change. The current MDL can be located in the LIMS. See HEAL QAP for more information on the appropriate determination of the MDL.

4.0 Definitions

- 4.1. Continuing Calibration Verification (CCV) – Standard from the same source as calibration curve. Used to check the stability of the instrument.
- 4.2. DI H₂O (DI) – De-ionized water/reagent free water. Water that is passed through a purification system and is free from interferences.
- 4.3. Initial Calibration Verification (ICV) - Second source standard used to determine the state of calibration of an instrument between periodic calibrations.
- 4.4. Laboratory Control Spike (LCS) – Laboratory fortified blank.
- 4.5. Matrix Spike (MS) – A laboratory fortified sample.
- 4.6. Matrix Spike Duplicate (MSD) – A laboratory fortified sample duplicate.
- 4.7. Method Blank (MB) – A laboratory blank.

5.0 Interferences

- 5.1. Salts of weak organic acids and inorganic acids, present in large amounts, may cause interference in electrometric pH measurements.
- 5.2. Oil and grease present in samples may coat the electrode and hinder the electrometric response.
- 5.3. When using the Metrohm Autotitrator, particulate material may cause interferences with the pH electrode and cause blockages in the instrumentation plumbing. When preparing samples for analysis it is recommended that particulate material be avoided.
- 5.4. Temperature of the sample(s) being analyzed can cause interference with the pH electrode. Samples should be allowed to equilibrate to room temperature prior to analysis. The pH electrode used must correct for temperature differences.

6.0 Safety

- 6.1. For handling procedures and exposure information always refer to the MSDS. To keep exposure to reagents and standards to a minimum, analysts must wear appropriate laboratory safety attire when working in the laboratory.
- 6.2. Refer to the current HEAL Health and Safety Manual.

7.0 Apparatus and Materials

7.1. Metrohm Autotitrator

- 7.1.1 855 Robotic Titrosampler equipped with:
 - 7.1.1.1 1-50mL 807 Dosino dosing unit
 - 7.1.1.2 1-20mL 807 Dosino dosing unit with 2L bottle
 - 7.1.1.3 772 peristaltic pump unit
 - 7.1.1.4 pH combination electrode
 - 7.1.1.5 Conductivity combination electrode
 - 7.1.1.6 Tiamo software for operation and data collection
- 7.1.2 50mL graduated cylinder.\
- 7.1.3 50mL disposable digestion vessels from Environmental Express.
- 7.1.4 60mL disposable plastic autosampler cups.

7.2. Bench-top pH meter.

7.2.1 VWR Symphony Benchtop pH Meter, Model SB70P equipped with:

7.2.1.1 VWR Symphony epoxy body pH electrode.

7.2.1.2 Separate VWR epoxy body temperature electrode.

7.2.2 50mL graduated cylinder.

7.2.3 50mL disposable digestion vessels from Environmental Express.

7.2.4 Magnet stirrer and Teflon stir-bars.

7.2.5 Class A 50mL burette.

7.2.6 Class A 10mL micro-burette.

7.2.7 Class A 200mL volumetric flask

7.2.8 Disposable plastic 4oz Solo cups.

7.2.9 Glass 150mL beakers.

8.0 Reagents, Standards, and Spikes

8.1. DI H₂O.

8.2. Sulfuric Acid, Standardized, 0.02000N.

8.3. Alkalinity Spike solution

8.3.1 Stock Alkalinity solution: Dissolve 0.848g of Na₂CO₃ (dried at 250°C for two hours and cooled in a desiccator) into 200mL DI water. This is a 4000 mg/L as CaCO₃ stock solution.

8.3.2 Spike 1mL into LCS, MS, and MSD samples. Report spike results as total alkalinity only. In LCS, MS, and MSD the spike concentration is 80 mg/L as CaCO₃.

8.4. pH Buffers

8.4.1 Primary standards: 1.68, 4.00, 7.00, 10.00, 12.45 for calibration of pH meter.

8.4.2 Second source standard: pH 7.00 only.

9.0 Sample collection, Preservation, and Storage

- 9.1. Samples are to be collected in unpreserved plastic or glass containers. Samples are stored at above freezing to 6°C until analysis.
 - 9.2. Holding time is 14 days.
 - 9.3. Samples should be removed from the storage refrigerator at least 2 hours prior to analysis to allow samples to equilibrate to room temperature.
- 10.0 Quality Control
- 10.1. Initial Calibration
 - 10.1.1 Methrohm Autotitrator: A 5 point calibration curve using all five pH buffers is performed daily.
 - 10.1.2 Manual pH meter: A 3 point calibration curve using buffers 4.00, 7.00, and 10.00 is performed daily.
 - 10.1.3 An ICV is analyzed following calibration.
 - 10.2. Continuing Calibration
 - 10.2.1 A pH CCV is analyzed every 20 analysis and at the end of each analytical run.
 - 10.2.2 It is recommended that the CCVs are rotated between pH buffers 4.00, 7.00, and 10.00.
 - 10.3. Batch QC Requirements
 - 10.3.1 An analytical batch consists of a MB, LCS, MS, MSD, and up to 20 samples.
- 11.0 Calibration
- 11.1. Initial Calibration
 - 11.1.1 Both Manual and Automated alkalinity testing requires daily pH calibration.
 - 11.1.2 See the current HEAL pH SOP for calibration procedure for pH electrode and acceptance criteria.
 - 11.2. Continuing Calibration
 - 11.2.1 A pH CCV is analyzed every 20 analysis and at the end of each analytical run. CCVs for pH buffers should be rotated between 4.00, 7.00, and 10.00.
- 12.0 Sample Analysis

- 12.1. Automated titration using Metrohm Autotitrator - for 20mg/L and 2mg/L PQL alkalinities
 - 12.1.1 Remove samples from refrigerator and set them out on the counter for at least two hours before analysis.
 - 12.1.2 Print "Poseidon Analysis Summary" from LIMS, include completed summary in data pack.
 - 12.1.3 Prepare LCS, MS, and MSD samples in the following manner:
 - 12.1.3.1 Use 50mL Environmental Express digestion tubes.
 - 12.1.3.2 For LCS, fill digestion tube to the 50mL mark with DI water.
 - 12.1.3.3 Spike volume is 1mL. Perform calibration check on pipette and document 1mL on Autotitrator Analysis Summary Sheet.
 - 12.1.3.4 Using a 1mL pipette remove 1 mL DI from digestion tube.
 - 12.1.3.5 Spike 1mL Alkalinity spike in to digestion tube. Cap, shake, then transfer sample to a 60mL autosampler cup.
 - 12.1.3.6 For MS and MSD, fill digestion tube to the 50mL mark using a client sample.
 - 12.1.4 Use clean 60mL auto-sampler cups for calibration pH buffers, samples, batch QC, and CCVs.
 - 12.1.5 Calibrate Autotitrator according to the procedure outlined in the current HEAL pH SOP.
 - 12.1.6 Select the Workplace icon. Click on the *Determination Series* tab.
 - 12.1.6.1 Double click on the first line and choose the *Cond.-pH-alk 50mL* method from the scroll down menu.
 - 12.1.6.2 Enter the HEAL sample ID on ID1 line.
 - 12.1.6.3 Enter additional notes for sample on ID2 line.
 - 12.1.6.4 Enter the sample position number.
 - 12.1.6.5 Click the right scroll arrow on the bottom left of the window to advance to the next sample position.
 - 12.1.6.5.1 Repeat 12.1.4.2 to load additional samples into list.

- 12.1.6.6 Click *Apply*, and then *Close* when finished entering IDs for all desired analyses.
- 12.1.7 After sample list has been filled appropriately, and prior to analysis, the list should be printed. The list shall be used to ensure that samples are located in appropriate positions on the auto-sampler rack.
- 12.1.7.1 Click on *Sample table* and select *Print (PDF)*. This will generate a temporary PDF file.
- 12.1.7.2 Print the PDF file. Save the PDF file to the Sample list directory located on the desktop with the file name corresponding to the analysis date.
- 12.1.8 Once sample list is complete and has been printed, prepare and load samples according to the sample list. Using this sequence should reduce analyst error of loading the auto-sampler incorrectly.
- 12.1.9 Measure 50mL of sample in a graduated cylinder. Pour this into a 60mL disposable plastic beaker. Place samples in the auto-sampler tray in the appropriate sample positions.
- 12.1.9.1 Always load a MB and LCS prior to sample analysis.
- 12.1.9.1.1 Use 50mL DI H₂O for the MB.
- 12.1.9.1.2 Follow Section 7.1.7.2 for the spiking procedure of the LCS.
- 12.1.9.2 Avoid floating particulates as they can cause interferences with the electrode and causes blockages in the instrumentation plumbing.
- 12.1.10 Remember to load and analyze a MS and MSD for up to every twenty samples.
- 12.1.11 Click *Start* to begin analysis.
- 12.1.12 The auto-sampler rinses between each sample.
- 12.1.13 The aspiration line and conductivity probe on the robotic arm are rinsed three times between sample analyses.
- 12.1.14 Samples may require a “dilution” to prevent over flow from the titration beaker.
- 12.1.14.1 Use 20mL of sample instead of the routine 50mL of sample.
- 12.1.14.2 If over flow is still a concern, discuss with Technical Director the changing of the 0.02N H₂SO₄ to a higher normality, 0.2N H₂SO₄.

- 12.1.14.3 When changing to a different normality, the system must be prepped again to make certain lines are flushed. The analysis of an additional LCS is also required.
- 12.2. Procedure for 20mg/L and 2mg/L PQL alkalinities - manual
- 12.3. Memphis – manual titration with 50mL and 10mL burettes
 - 12.3.1 Calibrate the pH meter according to current HEAL pH SOP.
 - 12.3.1.1 All acceptance criteria listed in the current HEAL pH SOP must be meet.
 - 12.3.2 20mg/L PQL alkalinity
 - 12.3.2.1 Pour out old 0.02N H₂SO₄ titrant from 50mL burette and refill with fresh solution. Remove bubbles from burette tip and record volume in logbook.
 - 12.3.2.2 For MB measure 50mL DI H₂O using graduated cylinder.
 - 12.3.2.2.1 Add magnetic stir bar and gently stir sample.
 - 12.3.2.2.2 Immerse pH probe in solution. Be sure the bulb (and thermocouple if present) is fully immersed in solution. Do not allow the stir bar to hit probe tip.
 - 12.3.2.2.3 Allow pH to stabilize, record starting pH, burette volume, and titrate to pH 4.5 ±0.20 pH units. (For MB proceed very slowly, this will be a very small volume).
 - 12.3.2.2.4 Record ending pH and burette volume.
 - 12.3.2.3 For LCS measure 50mL DI H₂O using a graduated cylinder and pour into a clean plastic Solo cup.
 - 12.3.2.3.1 Using the 1mL pipette, remove 1mL of DI H₂O from Solo cup, get a new tip for the pipette, then spike 1mL of Stock Alkalinity solution (this will be the LCS).
 - 12.3.2.3.2 Add magnetic stir bar and gently stir sample.
 - 12.3.2.3.3 Immerse pH probe in solution. Be sure the bulb (and thermocouple if present) is fully immersed in solution. Do not allow the stir bar to hit probe tip.

- 12.3.2.3.4 Allow pH to stabilize, record starting pH, burette volume, and titrate to pH 4.5 ± 0.20 pH units.
- 12.3.2.3.5 Record ending pH and burette volume.
- 12.3.2.4 For samples, measure 50mL of un-mixed sample in graduated cylinder, and pour into plastic 4oz Solo cup.
 - 12.3.2.4.1 Samples with very high alkalinities may be diluted prior to titration. DO NOT dilute the sample in DI H₂O. Simply titrate less sample. Be sure there is enough sample to allow pH probe tip to be completely submerged. 20mL of sample is appropriate.
 - 12.3.2.4.2 If a sample with a very high alkalinity has not reached the pH 4.5 endpoint but the Solo cup is full, transfer Stir bar and sample to a clean 150mL beaker and continue titration to the endpoint.
 - 12.3.2.4.3 Add stir bar, begin mixing, and immerse probe.
 - 12.3.2.4.4 Allow pH to stabilize. Record pH.
 - 12.3.2.4.5 If pH is above 8.30, titrate to pH 8.30 ± 0.05 pH units. Record pH and burette volume.
 - 12.3.2.4.6 Continue titration of sample until pH 4.5 end-point is reached (± 0.20 pH units). Record pH and burette volume.
 - 12.3.2.4.7 Dump sample down the drain, dispose of plastic solo cup and rinse Teflon stir-bar with DI. Continue with the next sample.
- 12.3.2.5 For MS and MSD samples, measure 50mL of an un-mixed sample into a 50mL graduated cylinder, and pour into 4oz solo cup.
 - 12.3.2.5.1 Using the 1mL pipette, remove 1mL of MS sample from Solo cup, get a new pipette tip, and then spike 1mL of Stock Alkalinity solution. Begin titration immediately.
 - 12.3.2.5.2 Follow procedure above for the titration of a LCS. Repeat with MSD sample.

12.3.3 2.0mg/L PQL (low level alkalinity)

- 12.3.3.1 Low level alkalinity procedure is only used when requested by client. If low level alkalinity is requested the MB and any sample with a total

alkalinity <20mg/L must be titrated using low level alkalinity procedure.

- 12.3.3.2 Pour out old 0.02N H₂SO₄ titrant from 10mL micro burette and refill with fresh solution. Remove bubbles from burette tip and record volume in logbook.
- 12.3.3.3 Measure 50mL DI H₂O in graduated cylinder and pour into a Solo cup (this will be the MB).
- 12.3.3.4 Add magnetic stir bar and gently stir sample.
- 12.3.3.5 Immerse pH probe in solution. Be sure the bulb (and thermocouple if present) is fully immersed in solution. Do not allow the stir bar to hit probe tip.
- 12.3.3.6 Allow pH to stabilize, record starting pH, and titrate to pH 4.5 ±0.20 pH units.
- 12.3.3.7 Allow pH to stabilize and record ending pH and burette volume. (Be very careful, this is a very small volume).
- 12.3.3.8 Continue titration to reduce the pH exactly 0.30 pH units. Record final pH and burette volume.
- 12.3.3.9 Repeat procedure using 50 mL of sample for any client samples that have <20 mg/L CaCO₃ (require less than 1 mL of titrant to reach endpoint pH 4.5)

13.0 Calculations

13.1. Total Alkalinity

$$\text{Total Alkalinity, mg / L CaCO}_3 = \frac{T \times N \times 50,000}{\text{mL of sample}}$$

Where:

T=Total mL of standard acid used for titration to pH 4.5 endpoint

N=Normality of standard acid

13.2. 2mg/L PQL - Low Level Alkalinity

$$\text{Total Alkalinity, mg / L CaCO}_3 = \frac{((2B) - C) \times N \times 50,000}{\text{mL of sample}}$$

Where:

B = mL titrant to first recorded pH (± 0.2 pH units from pH 4.5)

C = total mL titrant to reach 0.30 pH units lower (mL to approx. pH 4.5 plus 0.30 ph units lower)

13.3. Calculation of Alkalinity Relationships

13.3.1 Alkalinity relationships are calculated with the assumption that the total alkalinity only consists of the sum of bicarbonate, carbonate, and hydroxide alkalinities. Other weak acids that may contribute to the total alkalinity are not included in the calculation of the alkalinity relationships.

13.3.2 These relationships are determined by examining the relationship between the volume of titrant used to reach the pH 8.3 endpoint (also known as the phenolphthalein endpoint or P) and the total volume of titrant (including the volume used to reach pH 8.3 endpoint) used to reach the pH 4.5 endpoint (also known as T).

P = mL titrant to reach pH 8.3.

T = total volume of titrant used to reach pH 4.5.

13.3.3 In this SOP the alkalinity relationships shall be called: Bicarbonate/Carbonate, Carbonate, and Carbonate/Hydroxide.

13.3.4 The sum of bicarbonate, carbonate, and hydroxide alkalinities must always equal that of the total alkalinity calculated in 13.1.

13.3.5 Calculation of Bicarbonate/Carbonate Alkalinity

Where $P = 0$ or $P < 1/2 T$.

Hydroxide: $OH^- (mg CaCO_3 / L) = 0$

Carbonate: $CO_3^{2-} (mg CaCO_3 / L) = \frac{(2 \times P \times 50,000 \times N)}{V}$

Bicarbonate: $HCO_3^- (mg / L CaCO_3 / L) = \frac{(T - 2 \times P) \times 50,000 \times N}{V}$

Where:

P = mL of titrant to pH 8.3

T = Total mL of titrant to pH 4.5

N = normality of titrant

V = volume of sample in mL

13.3.6 Calculation of Carbonate Alkalinity

Where $P = 1/2 T$.

$$\begin{aligned} \text{Hydroxide:} \quad & OH^{-}(\text{mg } CaCO_3 / L) = 0 \\ \text{Carbonate:} \quad & CO_3^{2-}(\text{mg } CaCO_3 / L) = \frac{2 \times P \times 50,000 \times N}{V} \\ \text{Bicarbonate:} \quad & HCO_3^{-}(\text{mg } CaCO_3 / L) = 0 \end{aligned}$$

Where:

P = mL of titrant to pH 8.3

N = normality of titrant

V = volume of sample in mL

13.3.7 Calculation of Carbonate/Hydroxide Alkalinity

Where $P > \frac{1}{2} T$ or $P = T$

$$\begin{aligned} \text{Hydroxide:} \quad & OH^{-}(\text{mg } CaCO_3 / L) = \frac{(2 \times P - T) \times 50,000 \times N}{V} \\ \text{Carbonate:} \quad & CO_3^{2-}(\text{mg } CaCO_3 / L) = \frac{2(T - P) \times 50,000 \times N}{V} \\ \text{Bicarbonate:} \quad & HCO_3^{-}(\text{mg } CaCO_3 / L) = 0 \end{aligned}$$

Where:

P = mL of titrant to pH 8.3

T = Total mL of titrant to pH 4.5

N = normality of titrant

V = volume of sample in mL

13.4. Calculation for Total and Free CO₂ mg/L

13.4.1 Free CO₂

$$\text{free } CO_2(\text{mg } / L) = 2 \times B \times 10^{(6 - \text{sample } pH)}$$

Where:

B = Bicarbonate Alkalinity (HCO₃⁻ (mg CaCO₃/L))

13.4.2 Total CO₂

$$\text{total } CO_2(\text{mg } / L) = \text{free } CO_2(\text{mg } / L) + (0.44((2 \times B) + C))$$

Where:

B = Bicarbonate Alkalinity (HCO₃⁻ (mg CaCO₃/L))

C = Carbonate Alkalinity (CO₃²⁻ (mg CaCO₃/L))

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13.4.3 The report generated by Poseidon automatically calculates the Free CO₂ and Total CO₂ for all alkalinity determinations.

13.4.3.1 When reporting CO₂, one sample per batch must be hand calculated.

13.4.4 CO₂ calculations are done using the manual titration procedure only when requested.

13.4.4.1 These values are calculated by using a locked Excel spreadsheet. The calculated values are then transferred into the LIMS.

13.4.4.2 One sample per batch must be hand calculated.

14.0 Method Performance

14.1. PT or “blind study” samples are routinely analyzed to check the accuracy of the total alkalinity analysis.

14.2. MDL studies are done at a minimum of yearly. MDLs are completed the automated procedure only, and must be prepared and analyzed over a minimum of three days. Additional procedural requirements and the associated formulas can be found in the QAP.

14.3. A PQL check is performed yearly for the manual procedure.

14.4. MS/MSD limits will be established annually by control charting of MS/MSD recoveries.

15.0 Estimation of Uncertainty

15.1. Estimation of uncertainty is to be done on an annual basis.

15.1.1 Collect, at least, 20 of the most recent LCS data points. Calculate the standard deviation (s) and the average of all the readings. Calculate the 95% confidence interval (2 times the standard deviation). Report the estimated uncertainty as $\pm 2(s)$. Uncertainty data is kept on file in the method folders in the quality control office. See current revision of QAP for the formulas required to calculate uncertainty.

16.0 Demonstration of Capability (DOC)

16.1. Demonstration of Capability (DOC) samples are analyzed before an analyst is able to independently generate data.

16.2. DOCs for total alkalinity consist of four replicate spikes.

16.3. A detailed description of DOCs can be found in the HEAL QA Plan.

- 16.4. See the current HEAL QAP for necessary calculation and statistical requirements for DOC studies.
- 16.5. Annual Documentation of Continued Proficiency (ADOCP) is performed annually after acceptable DOC has been established. See HEAL Quality Assurance Plan.

17.0 Pollution Prevention

- 17.1. Standard 0.02N H₂SO₄ titrant comes pre-made and standardized. No preparation or standardization is necessary.
- 17.2. The automated titration system uses more pH buffer volume. However, using this system currently allows for at least three determinations to be done on a single aliquot of sample.

18.0 Data Assessment and Acceptance Criteria for Quality Control Measures

- 18.1. See **Appendix A** for a summary of batch QC requirements.
- 18.2. Total alkalinity value can be found on the generated report. The software calculates all necessary values. These values are based on a 50mL sample size. If a different sample volume was used, the value must be corrected.

18.3. pH Endpoints

- 18.3.1 The acceptable range for pH 8.3 endpoint is ± 0.05 pH units.
- 18.3.2 The acceptable range for pH 4.5 endpoint is ± 0.20 pH units
- 18.3.3 The acceptable range for additional 0.30 pH units for low level alkalinities is ± 0.05 pH units.

18.4. Batch QC

- 18.4.1 The MB must calculate to ≤ 20 mg/L when reporting to the 20mg/L PQL.
 - 18.4.1.1 Use the *Total Alk* value from the report.
- 18.4.2 The MB must calculate to ≤ 2 mg/L when reporting to the 2.0mg/L PQL.
 - 18.4.2.1 Use the *Low Level Titration* value from the report.
- 18.4.3 The LCS must be recovered to within $\pm 20\%$ of the assigned value.
- 18.4.4 The MS and MSD must be recovered within control charted limits.
- 18.4.5 The RPD for the MSD must be $\leq 20\%$.

18.5. Continuing Calibration Verification

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18.5.1 pH CCV must pass within ± 0.1 pH units.

19.0 Corrective Actions for Out-of-Control Data

19.1. pH Endpoint

19.1.1 If sample is titrated to a pH greater than the required endpoint, add additional titrant to bring pH into the acceptable range. If the sample has been titrated to less than the required endpoint (pH overshoot), the sample must be discarded and re-titrated.

19.2. Batch QC

19.2.1 If the MB calculates >20 mg CaCO_3 , reanalyze using fresh DI from a different location (i.e. any DI pump dispenser or wash bottle containing DI).

19.2.1.1 For low level alkalinities the MB must calculate to less than or equal to 2.0mg/L.

19.2.1.2 If MB is failing this may be an indication that the DI water system may not be producing ultra-pure water. Notify the Inorganic manager immediately. If MB continues to fail discontinue analysis until to source of the problem is fixed.

19.2.2 If the LCS fails, re-spike and reanalyze. If the spike continues to fail, remake stock spiking solution, spike and reanalyze. If it continues to fail discontinue analysis until the source of the problem can be fixed. The LCS value must be blank corrected.

19.2.3 If MS or MSD fails, re-spike and reanalyze. If spike continues to fail, flag data and report.

19.2.4 If RPD for MSD fails. Re-spike and reanalyze both MS and MSD, report reanalysis. If RPD is still out flag data and report.

19.3. Continuing Calibration Verification

18.3.1. If pH CCV fails, all alkalinity samples to the surrounding the failing CCV must be reanalyzed to the next acceptable CCV.

20.0 Contingencies for Handling Out of Control Data

20.1. All out of control data is flagged and reported to the client.

20.2. Corrective actions shall be filled out when there are deviations from the method or this SOP.

21.0 Waste Management

21.1. Analytical results are used to characterize their respective sample contamination level(s) so that the proper disposal can be performed. These wastes will be disposed of according to their hazard as well as their type and level of contamination. Refer to the Hall Environmental Analysis Laboratory Chemical Hygiene Plan for details regarding waste disposal.

22.0 References

22.1. Standard Methods 20th Edition, Method 2320B.

22.2. Standard Methods 20th Edition, Method 4500-CO₂ C.

22.3. Quality Assurance Plan, HEAL.

22.4. Chemical Hygiene Plan, HEAL.

22.5. Health and Safety SOP, HEAL.

22.6. Tiamo Software, Online Help, Metrohm.

Appendix A
Standard Methods 2320B: Total Alkalinity, Carbonate, Bicarbonate, and Hydroxide in Aqueous Samples
Corrective Action Procedures

Analytical Method	Parameter	QC Element	Frequency	Acceptance Criteria	Corrective Action
SM2320B	Wet Chemistry	pH Endpoint (8.30)	every sample, including QC	±0.05 pH units	1. If pH is "overshot" sample must be re-filtrated
		pH Endpoint (4.50)	every sample, including QC	±0.20 pH units	1. If pH is "overshot" sample must be re-filtrated
		Method Blank	1 per preparation/analysis batch (≤ 20 samples)	≤ PQL	1. Reanalyze using fresh DI from a different source. 2. Discontinue analysis.
		Laboratory Control Sample (LCS)	1 per preparation/analysis batch (≤ 20 samples)	% Recovery +/- 20% of actual value	1. Re-spike and reanalyze. 2. Remake spike solution. Respike and reanalyze. 3. Discontinue analysis.
		Matrix Spike (MS)	1 per preparation/analysis batch (≤ 20 samples)	% Recovery within control charted limits	1. Re-spike and reanalyze. 2. Flag data and report.
		Matrix Spike Duplicate (MSD)	1 per preparation/analysis batch (≤ 20 samples)	% Recovery within control charted limits Relative percent difference (RPD) ≤ 20%	1. MSD recovery: Re-spike and reanalyze. 2. MSD recovery: Flag data and report. 3. RPD: Re-spike and reanalyze both MS and MSD, report reanalysis. 4. RPD: Flag data and report.
		Continuing Calibration Verification (CCV)	1 per every 20 new samples	±0.1 pH units of actual value	1. All previous 20 new samples, and following 20 new samples must be reanalyzed to the next passing CCV