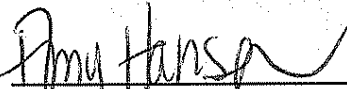


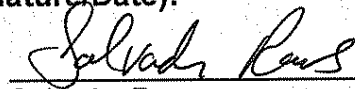
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Methods: EPA 310.1/ SM2320 B

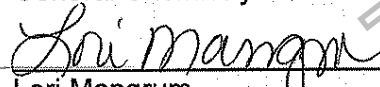
Approvals (Signature/Date):

 2/17/09

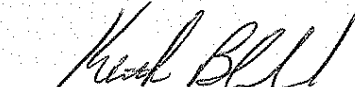
Amy Hansen
Department Manager
General Chemistry
Date

 2/18/09

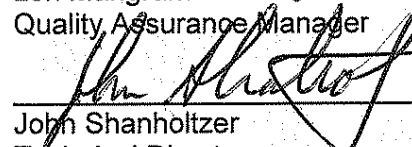
Salvador Ramos
Health & Safety Manager / Coordinator
Date

 2/23/09

Lori Mangrum
Quality Assurance Manager
Date

 2/17/09

Keith Blanchard
Laboratory Director
Date

 02-18-09

John Shanholtzer
Technical Director
Date

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1.0 SCOPE AND APPLICATION

- 1.1 This method is applicable to the determination of alkalinity in drinking, surface and saline waters, and domestic and industrial wastes.
- 1.2 The reporting limit for this SOP is 1.0 mg/l as CaCO_3 . No MDL study has been performed on this method.
- 1.3 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in the Methods Limit Group (MLG) in TestAmerica Tampa's LIMS (TALS).

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 20 in Tampa's Quality Assurance Manual.

2.0 SUMMARY OF METHOD

- 2.1 An unaltered sample is titrated to an electrometrically-determined endpoint of pH 4.5 or 4.2 for low alkalinities. The sample must not be filtered, concentrated, or altered in any way.
- 2.2 The phenolphthalein alkalinity may also be determined by titrating to an endpoint of 8.3.
- 2.3 This SOP also can be used to calculate the concentrations of various forms of carbonate species from the total alkalinity and the initial pH of the sample: carbonate, bicarbonate, hydroxide alkalinity, total CO_2 , and free CO_2 .
- 2.4 This SOP is based on EPA Method 310.1 and Standard Methods 2320B, 21st Edition.
- 2.5 Methyl Orange alkalinity is titrated to an endpoint of pH 3.7.

3.0 DEFINITIONS

Refer to TestAmerica Tampa SOP TP-AN-005: Definitions, Terms, and Acronyms and to the current revision of the Tampa's Quality Assurance Manual (TP-QAM) for a complete listing of applicable definitions.

- 3.1 Definitions: The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.1.1 Alkalinity - The sum of all titratable bases. Alkalinity of water is its acid-neutralizing capacity.

3.1.2 Analytical Batch - The set of sample extracted/distilled/or digested at the same time to a maximum of 20 samples.

3.1.3 Method Blank (MB) - A volume of deionized water in the same matrix as a quality control measure, but without the analyte analysed before the first sample.

3.1.4 Laboratory Control Standard/Duplicate (LCS/LCSD) – a standard used to measure the accuracy of a procedure. This standard is analyzed in duplicate.

* **NOTE:** A laboratory control sample duplicate (LCSD) is performed only when there are samples for a TMDL project included in the batch.

3.1.5 Laboratory Duplicate (DUP) - Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures. One duplicate sample is analyzed per every 10 samples.

3.1.6 Method Detection Limit (MDL) - The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero.

3.1.7 Practical Quantitation Limit (PQL) - Is the lowest point at which an analyte can be quantitated with at a specific degree of confidence and with accuracy and precision guidelines.

3.1.8 Reporting Limit (RL) - Is based on the PQL and defined by the laboratory. The RL should minimally be at or above the PQL.

4.0 INTERFERENCES

- 4.1 The pH electrode can become coated with oil or dirt. It is essential that the cell be thoroughly rinsed and, if necessary, cleaned well with a lint-free cloth and detergent between samples. Alternatively, the cell can be cleaned with 1:1 isopropanol and 10 N HCl.
- 4.2 Exposure to the atmosphere will cause an upward drift in samples with low conductivity due to the adsorption of carbon dioxide.

5.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 SPECIFIC SAFETY CONCERNS OR REQUIREMENTS

There are no specialized safety concerns associated with this method.

5.2 PRIMARY MATERIALS USED

There are no materials used in this method that have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

6.0 SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

- 6.1 Samples are unpreserved, do not filter, dilute, concentrate or alter the sample.
- 6.2 Samples are stored in plastic or glass containers at $\leq 6^{\circ}\text{C}$.
- 6.3 The holding time is 14 days from sampling through completion of analysis.

7.0 EQUIPMENT AND SUPPLIES

- 7.1 pH Meter and Electrodes with Temperature Compensation
- 7.2 Beakers
- 7.3 Stirring Apparatus and Stir Bars
- 7.4 Graduated Cylinders
- 7.5 Class A 25 ml buret

8.0 REAGENTS AND STANDARDS

- 8.1 Deionized water (ASTM type II),
- 8.2 Reagents:
 - 8.2.1 All reagents are labeled with their unique ID, the name of the material, the concentration, the date prepared and the expiration date. Reagent preparation is documented in the LIMS.
 - 8.2.2 Sulfuric Acid Titrant, 0.02 N, purchased commercially.
Standardize sulfuric acid by using 5 mls of sodium carbonate 0.05N to 100 mls of deionized water. Titrate to endpoint 4.5. Repeat this step 2 times.

Normality calculation: $\frac{5 \times 0.05}{\text{Volume of acid titrated}} = \text{N}$
 - 8.2.3 Sodium Carbonate Solution, 0.050 N, purchased commercially.

8.3 Standards:

- 8.3.1 All standards are labeled with their unique ID, the name of the material, the concentration, the date prepared and the expiration date. Standard preparation is documented in the LIMS.
- 8.3.2 Sodium Carbonate Solution, 0.050N. Take 5 ml into a 100ml flask and dilute to volume. Solution should equal 118 mg/l as CaCO_3 .
- 8.3.3 Calibration Standards purchased commercially.
- 8.3.4 pH Buffers: 4, 7, and 10

9.0 QUALITY CONTROL

- 9.1 **Sample QC** - The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Method Blank (MB)	1 in 20 or fewer samples	< MDL
Laboratory Control Sample (LCS)	1 in 10 or fewer samples	Statistical Limits ¹
Laboratory Control Sample (LCSD)*	1 in 10 or fewer samples	Statistical Limits ¹
Sample Duplicate	1 in 10 or fewer samples	Statistical Limits ¹

* LCS Duplicate (LCSD) is performed only when there are samples for a TMDL project included in the batch.

¹ Statistical control limits are updated annually and are updated into LIMS.

9.1.1 Each analytical batch may contain up to 20 samples, a Laboratory Control Sample (LCS), a Duplicate (LCSD) and a sample duplicate per every ten samples. Matrix Spikes are not analyzed for this analysis.

* **NOTE:** A laboratory control sample duplicate (LCSD) is performed only when there are samples for a TMDL project included in the batch.

9.1.2 Method Blank. No target analytes may be present in the method blank above the reporting limit. The prescribed corrective action is reanalysis of the Method Blank to confirm the contamination, which if it is confirmed, requires cleaning of the electrode and re-analysis of all associated samples.

9.1.3 The LCS consists of 0.05N sodium carbonate for alkalinity standard purchased commercially. All analytes must be within established control limits. If any analyte in the LCS is outside the laboratory established control limits, corrective action must occur, discuss with supervisor immediately. Corrective action may include reanalysis of the batch.

- 9.1.4 Instrument conditions must be the same for all standards, samples and QC samples
- 9.1.5 All data will be reviewed by the analyst (1st review level) and then by a peer or supervisor (2nd level review).
- 9.1.6 Record all analytical information in the analytical logbook or TALS including the analytical data from standards and any corrective actions or modifications to the method.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Calibrate the pH meter in accordance with the manual or SOP TP-GE-004.

10.2 Standardization of titrant:

- Calibrate the pH meter in accordance with TPA-GE-004.
- Fill the 10ml burette with the 0.02N sulfuric acid solution.
- Transfer 15.0mL of the ~0.05N sodium carbonate solution to a 100mL beaker and add a small stir bar.
- Place the beaker on the stir plate. Submerge the pH probe below the liquid. Do not allow the stir bar to hit the probe, as this will cause erratic readings.
- Add 5-6 drops of bromocresol green indicator. The color should be blue. (The indicator is added to help gauge the endpoint of the titration.)
- Titrate the sodium carbonate solution with the 0.02N sulfuric acid until the pH is 4.5. The indicator will turn pink near the endpoint. Titrate very slowly as the pH approaches 4.5.
- Record the volume of 0.02N sulfuric acid needed to reach the endpoint.

Repeat the titration two more times with fresh portions of 0.05N sodium carbonate solution.

$$\text{Normality} = \frac{A \times B}{C}$$

where:

- A = Normality of Ca_2CO_3 used
- B = ml of Ca_2CO_3 used
- C = mL acid used

-Average the three titrations to obtain the normality of the sulfuric acid solution used to calculate the alkalinity of the field samples and QC.

10.3 Documentation: All results are documented in the Alkalinity Logbook or in TALS.

11.0 PROCEDURE

- 11.1 Place 50 ml sample into beaker.
- 11.2 Begin stirring and measure initial pH of sample
- 11.3 Titrate the sample to an endpoint of 4.5 with 0.02N H₂SO₄.
 - 11.3.1 Samples which have <1000 mg CaCO₃/l, use 0.02N titrant
 - 11.3.2 Samples which have > 1000 mg CaCO₃/l, use 0.1N titrant
- 11.4 Samples requiring methyl orange alkalinity are titrated to an endpoint of pH 3.7.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 QC result evaluation:

12.1.1 Method Blank. No target analytes may be present in the method blank above the reporting limit. The prescribed corrective action is reanalysis of the method blank to confirm the contamination, which if it is confirmed, requires cleaning of the electrode and analysis of all associated samples.

12.1.2 Laboratory Control Sample (LCS): All analytes must be within established control limits. If any analyte in the LCS is outside the laboratory established control limits, corrective action must occur. Corrective action may include reanalysis of the batch. (90-110%)

12.2 Data review:

12.2.1 The entire data set will be reviewed by the analyst and supervisor (or designee) of the appropriate analytical section.

12.3 Calculations:

12.3.1 Equation 1: Calculation of Total Alkalinity.

$$\text{Alkalinity, mg Ca}_2\text{CO}_3\text{/L} = \frac{A \times N \times 50000}{\text{mL sample}}$$

where:

A = mL acid used

N = Normality of acid used

12.3.2 Equation 2: Calculation of Low Alkalinity.

$$\text{Alkalinity, mg Ca}_2\text{CO}_3/\text{L} = \frac{(2B - C) \times N \times 50000}{\text{mL sample}}$$

where:

B = mL acid used to pH 4.5

C = mL acid used to pH 4.2

N = Normality of acid used

12.3.3 Calculations of Alkalinity relationships.

Phenolphthalein alkalinity (P): present only when the initial pH is above 8.3.

Carbonate (CO_3^{2-}) alkalinity: present when phenolphthalein alkalinity is not zero but is less than the total alkalinity.

Hydroxide (OH^-) alkalinity: present if phenolphthalein alkalinity is more than half the total alkalinity.

Bicarbonate (HCO_3^-) alkalinity: present if phenolphthalein alkalinity is less than half the total alkalinity.

The following table shows the calculations for the different relationships of alkalinity:

Results of Titration	Hydroxide Alkalinity as CaCO_3	Carbonate Alkalinity as CaCO_3	Bicarbonate Alkalinity as CaCO_3
P=0	0	0	T
$P < \frac{1}{2} T$	0	2P	$T - 2P$
$P = \frac{1}{2} T$	0	2P	0
$P > \frac{1}{2} T$	$2P - T$	$2(T - P)$	0
$P = T$	T	0	0

P = phenolphthalein alkalinity; T = total alkalinity

12.3.4 Equation 3: LCS % Recovery. (90-110%)

$$\text{LCS \% Recovery} = \left(\frac{\text{Measured conductivity}}{\text{Theoretical conductivity}} \right) \times 100$$

12.3.5 Equation 4: Relative percent difference.

$$\text{RPD} = \left(\frac{|\text{Dup 1 Result} - \text{Dup 2 Result}|}{\text{Dup 1 Result} + \text{Dup 2 Result}} \right) \times 200$$

13.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QUALITY CONTROL MEASURES

The following represent data assessment for samples and acceptance criteria for QC measures. Corrective actions for any failure in QC must be discussed with supervisor and Project Manager as well as documented in an NCM.

QC sample acceptance criteria

- 13.1 Laboratory Control Sample (LCS/LCSD)- (90-110%) Alkalinity must be within established control limits for accuracy (%Recovery) in the laboratory LIMS Method Limits Group. Exceptions are allowed only with QA and department manager approval.
- 13.2 Duplicate Sample- (< 30) The duplicate sample must be within established control limits for precision (RPD) in the laboratory LIMS Method Limits Group. Exceptions are allowed only with QA and department manager approval.

14.0 CORRECTIVE ACTIONS FOR OUT OF CONTROL DATA

14.1 Laboratory control sample

- 14.1.1 If Alkalinity is out of control for accuracy (90-110%) (% Recovery), the associated samples are reanalyzed

14.2 Duplicate sample

- 14.2.1 If Alkalinity is out of control for precision, the sample and its duplicate must be reanalyzed.

15.0 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

15.1 LCS/LCSD

- 15.1.1 If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly discussed with the supervisor and Project Manager as well as documented in a Non Conformance Memo (NCM), in the project records and the report.
- 15.1.2 If reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

15.2 Insufficient sample

- 15.2.1 If there is insufficient sample to repeat the analysis, the project manager is notified via NCM for consultation with the client.

16.0 Method Performance

- 16.1 Each analyst must perform an Initial Demonstration of Capability (IDOC) in accordance with Tampa's SOP TP-CA-092: *Evaluation of IDOC's* prior to analysis of samples. *Ongoing Demonstration of Capability* (ODOC) must be performed annually.
- 16.2 Method validation – A Method Detection Limit study is not required for this method.

17.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to Tampa's current revision of SOP TP-HAZ-001 *Waste Management*.

There are no special waste streams associated with this method.

18.0 REFERENCES

- 18.1 EPA 310.1, Alkalinity,
- 18.2 Standard Methods for the Examination of Water and Wastewater, 21st Edition, Alkalinity, Method 2320B
- 18.3 TestAmerica's Environmental Health & Safety Manual CW-E-M-001, Most current revision
- W
- 18.4 TestAmerica Tampa Quality Assurance Manual, current revision.
- 18.5 TestAmerica Tampa SOP's:
- 18.5.1 TP-HAZ-001 Waste Management,
 - 18.5.2 TP-AN-006 Analytical Batching
 - 18.5.3 TP-CA-092 Evaluation of IDOC's
 - 18.5.4 TP-HAZ-001 Waste Management
 - 18.5.5 TP-GE-004 pH SM4500H+B
 - 18.5.6 TP-AN-005: Definitions, Terms, and Acronyms

19.0 REVISION HISTORY

- Revision 2, dated 01 March 2009
 - Removed references to STL and updated to TestAmerica format
 - Updated references, added all SOP's and documents referenced within SOP
 - Added revision history section
 - Rewrote procedure for manual not instrument titration
 - Added Methyl Orange titration endpoint

UNCONTROLLED