APPENDIX D: BABCOCK LABORATORY

METHOD #: EPA 300.0, and 9056
SM 4110 B
CA DHS IC Rev 0

TITLE: The Determination of Inorganic Anions in Water by Ion Chromatography

ANALYTE:	CAS #
Chloride Cl	7782-50-5
Fluoride F	7782-41-4
Nitrate (NO_3)	
Nitrite (NO_2)	
Phosphate (PO_4)	
Sulfate (SO_4)	
Perchlorate (ClO_4)	
Para-Chlorobenzene Sulfonic Acid (PCBSA)	

INSTRUMENTATION:

IC: Dionex 500DX and 120DX (see sec. 6.2)
Data Handling: Pentium Processor with Peak-Net software on Windows NT platform.
Printer: HP Laser Jet 2100
Autosampler: Alcott Micromeritics 728

1.0 Scope and Application

1.1. This method covers the determination of the following inorganic anions.

		RL, mg/L
1.1.1. Method A.		
1.1.1.1.	Fluoride	0.1
1.1.1.2.	Chloride	1
1.1.1.3.	Nitrate-N	0.2
1.1.1.4.	Nitrite-N	0.1
1.1.1.5.	Phosphate-P	0.05
1.1.1.6.	Sulfate	0.5
1.1.1.7.	PCBSA	10
1.1.2. Method C		
1.1.2.1.	Perchlorate	0.004

Note: RL = Reporting Limit

1.2. The matrices applicable to each method are shown below:
1.2.1. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 2.3),
1.2.2. Drinking water and reagent waters.

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1.2.3. Drinking water, groundwater and reagent waters.

1.3. The Single Laboratory Method Detection Limit (MDL, defined in section 13.1) for the above analytes is listed in Tables 1A through 1C. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4. The working range for these analytes is as follows:

1.4.1.	Fluoride	0.1-5 mg/L
1.4.2.	Chloride	1-250 mg/L
1.4.3.	Nitrate-N	1-250 mg/L
1.4.4.	Nitrite-N	0.1-5.0 mg/L
1.4.5.	Phosphate-P	0.05 -5.0 mg/L
1.4.6.	Sulfate	1-400 mg/L
1.4.7.	Perchlorate	0.004-0.25 mg/L
1.4.8.	PCBSA	1-500 mg/L

1.5. This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.6. When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.9.

2. Summary of Method

2.1. An aliquot Sample (25 µL for Method A, and 740 µL for Method C)of sample is injected into an eluent stream and passed through a series of ion exchangers. The system is comprised of a guard column, separator column, and suppressor device. These separate the ions based on their affinity for a low capacity, strongly basic ion exchanger. They are then directed onto a strongly acidic cation exchanger where they are converted to their highly conductive acidic forms. The conductivity of these acid forms is measured. Identification is based on retention time. Quantitation is based on peak height or peak area.

2.2. The main differences between Method A and C are the separator columns, guard columns and eluents. Sections 6 and 7 will elicit the differences.

2.3. In order to use this method for solids an extraction procedure must be performed (See Sec 11.10).

3. Definitions (see SOP Q15 for further definitions)

3.1. Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte. Stock standard solutions are used to prepare calibration standards.

3.2. Calibration standards (CAL) - a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed and used to calibrate the instrument response with respect to analytic concentration.

3.3. Quality control sample (QCS) - a solution containing known concentrations of analytes, received quarterly from an outside vender (such as ERA). The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4. Performance evaluation sample (PE) - a solution of method analytes acquired from an outside source. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Analyte true values are unknown to the analyst.

3.5. Initial Calibration Check ICC (or Calibration Check standard) - a solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water used to evaluate the performance of the instrument system right after a calibration is performed. The low-level calibration standard is reinjected as well as the LCS to satisfy this requirement.

3.6. Laboratory duplicates (DUP) - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7. Laboratory fortified sample matrix (LFM) or Matrix Spike (MS) - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM (or MS) is analyzed

exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM (or MS) corrected for background concentrations.

3.8. Laboratory Control Sample (LCS) referenced in the method for oxyhalides as the Continuing Calibration Check and in the method for perchlorates as the Laboratory Fortified Blank and Instrument Performance Check. An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control.

3.9. Reporting Level Check A standard is run daily at the reporting limit to demonstrate that the laboratory is capable of making accurate and precise measurements at the required reporting detection limit (a). Once a year this standard is run seven times in a row as part of a detection limit study (b).

3.10. Method Blank (MB) An aliquot of D.I. water is analyzed at the beginning of a run and every ten samples.

4. Interferences

4.1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.2. The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4. Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems. Caution: filtration may remove perchlorate.

4.5. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7. The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

5. Safety

5.1. Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

5.2. See SOP S01 , Concentrated Acids and Bases
SOP S02 – Compressed Gas Cylinder Handling
SOP S03 – Spill Control Policy

6. Apparatus and Materials

6.1. Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2. Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1. Anion guard column: A protector of the separator column. If omitted from the system the retention limes will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2. Anion separator column:
6.2.2.1. Anion separator column (Method A):

6.2.2.1.1. AS-4A 4mm Dionex Column
6.2.2.1.2. AG4A 4mm Dionex Guard Column
6.2.2.2. Anion separator column (Method C):
6.2.2.2.1. AS-5 Dionex Column
6.2.2.2.2. AG-5 Dionex Guard Column
6.2.3. Anion suppressor column:
6.2.3.1. Anion suppressor column (Method A): Anion self-regenerating ASRS-11.
6.2.3.2. Anion suppressor column (Method C): Anion micromembrane suppressor AMMS-11
6.2.4. Detector – CD20 conductivity cell.

7. Reagents and Consumable Materials

7.1. Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2. Reagent water: Nanopure, free of the anions of interest. Water should contain particles no larger than 0.20 microns with a conductance of <0.1uS/cm.

7.3. Eluent solution:
7.3.1. Method A: Dissolve 0.571 g sodium bicarbonate ($NaHCO^3$) and 0.763 g of sodium carbonate (Na^2CO^3) in 1 liter of nanopure water (7.2) and dilute to 4 liters.
7.3.2. Method C: Add 19.2 mL of 50% NaOH and 0.4765 g of 4-cyanophenol to 1 liter of nanopure water (degassed by Nanopure process DHS-IC-Rev 0 7.2). Dilute to 2 liters.

7.4. Regeneration solution (MicroMembrane Suppressor) Concentrated Sulfuric Acid:
7.4.1 Method C: 3.9 mL per 4 liters nanopure water.

7.5. Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4-C. The bottle expiration dates are used as a guideline. Dilute working standards should be prepared each time a calibration is performed. LCS solutions are prepared weekly except those that contain phosphate which are prepared fresh daily (c).

8. Sample Collection, Preservation and Storage

8.1. Samples should be collected in scrupulously clean glass or polyethylene bottles.

8.2. Sample preservation and holding times for the anions that can be determined by this method are as follows.

Analyte	Preservation	Holding Time
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N/Nitrite-N		
Unchlorinated	Cool to 4°C	48 hours
chlorinated	Cool to 4°C	14 days
combined	conc. H_2SO_4 pH < 2	28 days
o-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days
Perchlorate	Cool to 4°C	28 days
PCBSA	Cool to 4°C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4-C and held no longer than 28 days for Method A or Method C.

9. Calibration and Standardization
(See Standard Logs for recipes of all standards.)

9.1. Establish ion chromatographic operating parameters equivalent to those indicated in Table 1A or 1B.

9.2. For each analyte of interest, prepare calibration standards at a minimum of three concentration levels (five for method C) by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. The curve is forced through the 0 point. An acceptable curve has a $r^2 \geq 0.995$. A method blank is analyzed after the calibration to verify this point (d). If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration

concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

9.3. Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

9.4. The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than the range indicated under CCV standards, the test must be repeated, using fresh calibration standards. If the results are still out of range, a new calibration curve must be prepared for that analyte.

ICV Standards

	Analyte	Conc.	Acceptance Range %
Method A:			
	Cl	150ppm	90-110
	NO_3	111ppm	90-110
	SO_4	250ppm	90-110
	F	2ppm	90-110
	NO_2	2ppm	90-110
	PO_4	2ppm	90-110
Method C:	ClO_4	25ppb	90-110

CCV Standards

	Analyte	Conc. Mid	Conc. High	Acceptance Range %
Method A:				
	Cl	10	150ppm	90-110
	NO_3	44.3	111ppm	90-110
	SO_4	30	250ppm	90-110
	F	0.5	2.0ppm	90-110
	NO_2	0.5	2.0ppm	90-110

	PO_4	0.5	2.0ppm	90-110
Method C:	ClO_4	125	250ppb	90-110

Calibration Standards

Method A:

Std #1				Std #4			
Cl	1ppm	F	0.05ppm	Cl	100ppm	F	1.0ppm
NO_3	1ppm	NO_2	0.05 ppm	NO_3	150ppm	NO_2	1.0ppm
SO_4	1ppm	PO_4	0.05 ppm	SO_4	150ppm	PO_4	1.0ppm

Std #2				Std #5			
Cl	10ppm	F	0.1ppm	Cl	200ppm	F	2.0ppm
NO_3	25ppm	NO_2	0.1 ppm	NO_3	200ppm	NO_2	2.0ppm
SO_4	30ppm	PO_4	0.1 ppm	SO_4	350ppm	PO_4	2.0ppm

Std #3				Std #6			
Cl	20ppm	F	0.5ppm	Cl	250ppm	F	5.0ppm
NO_3	50ppm	NO_2	0.5 ppm	NO_3	250ppm	NO_2	5.0ppm
SO_4	60ppm	PO_4	0.5 ppm	SO_4	400ppm	PO_4	5.0ppm

PCBSA Std #1 1ppm, Std #2 5ppm, Std #3 10ppm
Std #4 50ppm, Std #5 100ppm

Method C:

ClO_4: Std #1 4ppb, Std #2 10ppb, Std #3 50ppb
Std #4 100ppb, Std #5 250ppb

Lab Controls

Method A:

Acceptance range 90% - 110%

Cl	High	150 ppm	Low	10ppm
NO_3	High	111 ppm	Low	44.3ppm
SO_4	High	250 ppm	Low	30ppm
F	High	2.0 ppm	Low	0.5ppm
NO_2	High	2.0 ppm	Low	0.5ppm
PO_4	High	2.0 ppm	Low	0.5ppm

PCBSA 25ppm Acceptance range 80% - 120%

Method C:

Acceptance range 80% - 120% (e)
ClO_4 25ppb

Matrix Spikes

Method A: No spikes analyzed (f). Duplicates are analyzed instead since these analytes are rarely none detected.

Method C:

Acceptance range: waters 80% - 120% max RPD 20
Soils 75% - 125% max RPD 35

ClO_4 12.5ppb X any prep or dilution factor

10. Quality Control

10.1. Our laboratory has a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of control samples as a continuing check on performance. The laboratory maintains performance records to define and document the quality of data that are generated.

10.1.1. In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2. 5 to 10% of all samples are run in duplicate.

10.2. Before performing any analyses, the analyst demonstrates the ability to generate acceptable accuracy and precision with this method using a laboratory performance standard. Each analyst will analyze four replicates of a standard that is ten times their most recently proven MDL. Method C perchlorate requires four replicates at 25ppb. The acceptance criteria for this study is 90 – 110% recovery for water matrices and 80 – 120% recovery for solid matrices (g).

10.3. The laboratory develops and maintains accuracy statements of laboratory performance for each matrix being analyzed by the laboratory

10.4. Before processing any samples, the analyst demonstrates through the analysis of an aliquot of D.I. water (MB) that all glassware and reagent interferences are under control. Each time there is a change in reagents, the MB is monitored for the appearance of negative peaks as a safeguard against laboratory contamination (h).

10.5. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification must be used.

10.6. Quality control check samples are analyzed concurrently with those performance evaluation sample studies required to maintain state certification.

10.7. For Method C (i), the linear calibration range is verified every 6 months or whenever a significant change in the instrument response is observed.

10.8. In order to verify that standards have been prepared correctly a LCS is performed using a standard of known concentration from an independent source. This laboratory control sample containing each analyte of concern is analyzed with each batch of samples processed. If more than 20 samples are run in a batch analyze one LCS for every 20 samples (10 for drinking water). Evaluate the accuracy by comparing to laboratory acceptance criteria. If acceptable data cannot be obtained, locate the problem and correct it. If during the course of a run a LCS is out of range, if possible it is rerun on the spot. If this is not possible the analyst may reevaluate the data based on peak height rather than peak area. If the data still does not fall within the acceptance criteria, the analyst may choose to use the six point calibration curve (for method A) to interpret the data rather than the three point lower level curve. If all the LCS' are in range under these conditions, the data is accepted. Otherwise a fresh calibration is performed and all samples are rerun starting from the last acceptable LCS.

11. Procedure

11.1. Set-up:

11.1.1. Prepare Eluant. Turn He valve to 5psi for method A and 30 psi for Method C. Check that the He line is connected to the eluant bottle. Set pump rate as per table 1.

11.1.2. On peaknet program – click on run icon. Under file click on load method. Method A – anion 300; Method C – a-clo4.met.
11.1.3. Wait for conductivity and pressure to stabilize.

11.2. Standardization and Calibration:
11.2.1. Using a clean syringe, fill one vial with the Method Blank.
11.2.1.1. Place vial in position #1 of autosampler.
11.2.1.2. Press <START> enter.
11.2.1.3. Init V <1> enter.
11.2.1.4. Rinse <0> enter.
11.2.1.5. Last V <1> enter.

11.2.2. Using a clean syringe, fill one vial with an initial calibration verification standard.
11.2.2.1. Place vial in position #2 of autosampler.
11.2.2.2. Press <START> enter.
11.2.2.3. Init V <1> enter.
11.2.2.4. Rinse <0> enter.
11.2.2.5. Last V <2> enter.
11.2.3. The initial calibration verification standard should read within the established control limits. If it does not, reinject it, if it still does not work, recalibrate.
11.2.3.1. Load calibration standards on the autosampler
11.2.3.2. Inject six calibration standards.
11.2.4. Check an initial calibration verification standard again.

11.3. Analysis:
11.3.1. Fill vials with sample, filtering (for Method A) through a 0.2 μm disc filter. For methods B & C, samples containing suspended material may be centrifuged or decanted.
11.3.2. Start the autosampler on vial 1 through 64.
11.3.2.1. Press <START> enter.
11.3.2.2. Init V <1> enter.
11.3.2.3. Rinse <0> enter.
11.3.2.4. Last V < # of last vial> enter.
Note: for method C, 2 vials per sample are loaded onto the autosampler.
11.3.3. Run continuing calibration verification standards every 10 samples. Run a lab control, method blank, and duplicate every 20 samples. Run matrix spikes every 20 samples for method B and C. Run a check standard at the end.
11.3.4. If a sample is above the high standard, dilute with D.I. water, according to the thickness and height of the peak. Make sure the peaknet software is calculating appropriately by observing peak heights and retention times.

11.4. Shutdown
- 11.4.1. Under Run – load stop method.
- 11.4.2. Turn pressure valve to 0 psi.

Note: Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.5. Check system calibration daily and, if required, recalibrate as described in Section 9.

11.6. Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.7. The computer software comes with default retention time window widths. This is used to make identifications unless experience shows that the window requires adjustment (j). The experience of the analyst weighs heavily in the interpretation of chromatograms.

11.8. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.9. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.10. The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This mixture is agitated for sixty minutes by shaking intermittently. Filter the resulting slurry before injecting using a 0.45 micron membrane type filter. With the exception of method C, this can be the type that attaches directly to the end of the syringe. Two samples per batch are spiked prior to extraction. These spikes are used to demonstrate that good recovery and identification of peaks is obtained with the users matrix.

12. Calculation

12.1. Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. The system will then compute sample concentration by comparing sample peak response with the standard curve.

12.2. Report results in mg/L.

12.3. Report:
NO_2^- as N
NO_3^- as N or as NO_3 if desired by the client
$H(PO_4)_2^-$ as P

13. Precision and Accuracy - Method Detection Limit

13.1. The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1A and 1B were obtained using reagent waters.

14. Calculations associated with this method:

14.1. Total Anions (TA)
mequiv. of OH + CO3 + HCO3 + SO4 + Cl + NO3 = TA

14.2. Electrochemical Balance (ECB)
Total Cations (TC) – Total Anions (TA)

14.3. Total Dissolved Solids by Summation (TDSSUM)
mg/L of 0.6(Total Alkalinity) + Na + K + Ca + Mg + SO4 + Cl + NO3 + F + SiO3 = TDSSUM

Table 1A. Chromatographic Conditions and Detection Limits In Reagent Water (Method A)

Analyte	Peak #	MDL (mg/L)
Fluoride	1	0.01
Chloride	2	0.792
Bromide	4	0.0015
Nitrate-N	5	0.0115
o-Phosphate-P	6	0.003
Sulfate	7	0.028
PCBSA	8	<1 (EDL)

Standard Conditions:

Unit:	DX 120
Columns:	as specified in 6.2.2.1
Detector:	as specified in 6.2.4
Pump Rate:	2.0 mL/min.
Eluent:	as specified in 7.3.1
Sample Loop:	25 uL

Table 1B. Chromatographic Conditions and Detection Limits In Reagent Water (Method C)

Analyte	MDL (mg/L)
Perchlorate	0.0018

Standard Conditions:

Unit:	DX500
Column:	as specified in 6.2.2.3
Detector:	as specified in 6.2.4
Pump Rate:	1.0 mL/min.
Eluent:	as specified in 7.3
Sample Loop:	740 uL

15.0 Corrective Action For Out of Control Or Unacceptable Data:

See SOP Q06 – Corrective Action

16.0 Pollution Prevention and Waste Management:

See SOP S05 – Neutralization Procedure for Acid and Alkaline Wastes
SOP S07 – Pollution Prevention

Method Variations

(a). Low Level Check Frequency EPA Method 300.0 section 10.8.
(b). Low Level Check Duplicates EPA Method 300.0 section 10.9.
(c). Stability of Standards - EPA Method 300.0 section 7.5.

(d). Blank in Calibration – EPA Method 300.0 section 9.2. and DHS-IC-Rev 0 section 10.2.
(e) LCS Acceptance Limit - California Department of Health Services IC Rev 0, section 9.3.2, 9.3.3.
(f). Laboratory Fortified Sample Matrix required for each method – EPA Method 300.0 revision 2.1, section 9.4.1.
(g) .Demonstration of Capability EPA Method 300.0 section 10.2.
(h). Reagent Water Monitoring EPA Method 300.0 section 10.5.
(i). Proof of Linear Calibration Range required for each method - EPA Method 300.0 revision 2.1, section 9.2.2.
(j). Retention Time Window – EPA Method 300.0 section 11.4.

References:

EPA SW846 method 9056

EPA Methods for the Determination of Inorganic Substances in Environmental Samples, Method 300.

California Department of Health Services IC Rev 0

Approved by Susann K Thomas 8/25/00

METHOD #: EPA 350.1, SM 4500-NH_3 H

TITLE: I53 Nitrogen, Ammonia (Colorimetric, Automated Phenate)

ANALYTE: Ammonia Nitrogen

1.0 Scope and Application

1.1 This method covers the determination of ammonia in drinking, surface, and saline waters, domestic and industrial wastes in the range of 0.1 to 5.0 mg/L NH3 as N. This range is for photometric measurements made at 630nm in a 10 mm tubular flow cell. Higher concentrations can be determined by sample dilution.

2.0 Summary of Method

2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to the ammonia concentration. The blue color formed is intensified with sodium nitroprusside.

3.0 Sample Handling and Preservation

3.1 Preservation by addition of conc. H_2SO_4 to a pH < 2 and refrigeration at 4-C.

3.2 Safety: Safety glasses and gloves should be worn when dealing with acids and bases.

4.0 Interferences

4.1 Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. A 5% EDTA solution is used to prevent the precipitation of calcium and magnesium ions from river water and industrial waste. For sea water a sodium potassium tartrate solution may be used.

4.2 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. Sample color that absorbs in the photometric range used will also interfere. Sample is diluted if necessary

4.3 Marked variation in acidity and alkalinity are eliminated by sample preservation with H_2SO_4. The pH is then checked to ensure that it is <2. (a) Due to the reducing nature of this environment, residual chlorine is not expected to be a problem. (b) The sample is neutralized prior to analysis by the addition of the first reagent which is a NaOH buffer. (c)

5.0 Apparatus

5.1 Test tube rack from Lachat.

5.2 13 x 100 mm disposable culture tubes.

5.3 Lachat Quikchem Analyzer

5.4 Whatman 2 and Whatman 4 (11.0 cm) filter paper or Gelmin 0.45 micron disk filters.

5.5 100 ml beakers.

5.6 1 ml, 2 ml, 5 ml, and 10 ml pipets.

5.7 25 ml, 50 ml, and 100 ml graduated cylinders.

5.8 Helium Gas (technical grade).

5.7 Digestion hot plates

6.0 Reagents (d)

6.1 Nanopure water

6.2 Carrier or preserved water: 2ml of Sulfuric acid dilute to 1 gallon with Nanopure. Degas with Helium just prior to analysis.

6.3 Sodium phenolate: Using a 1 liter Erlenmeyer flask, 88ml of 88% phenol in 500 mL of Nanopure water. In small increments, cautiously add with agitation, 32 g of NaOH. Periodically cool flask under water faucet. When cool, dilute to 1 liter with Nanopure water.

6.4 Sodium hypochlorite solution: Dilute 250 mL of a bleach solution containing 5.25% NaOCl (such as "Clorox") to 500 mL with Nanopure water. Available chlorine level should approximate 2 to 3%. Since "Clorox" is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of this product, storage over an extended period should be avoided.

6.5 Buffer: Disodium ethylenediamine-tetraacetate (EDTA) (5%): Dissolve 50 g of EDTA (disodium salt) and 9g of NaOH in 1 liter of Nanopure water. Degas with Helium just prior to analysis.

6.6 Sodium nitroprusside (0.05%): Dissolve 3.5 g of sodium nitroprusside in 1 liter of Nanopure water.

7.0 Standards:

7.1 Lab Control Sample (LCS) and Matrix Spikes (MS/MSD):

7.1.1 Stock Solution: EM 1000 mg/L NH_3 Standard.

7.1.2 LCS: Dilute 1 ml of stock to 1000 ml in a volumetric flask with preserved water (7.3). The concentration is 1 mg/L NH_3 or 0.78 mg/L NH_3-N

7.1.3 Acceptability: The result of the LCS analysis is compared to statistically generated acceptance ranges. If the analysis does not fall within the acceptance range,(85%-115%) the analysis is stopped until the cause is determined and the LCS is within the acceptance range.

7.2 Matrix Spike (MS) / Matrix Spike Duplicate (MSD)

7.2.1 Spike solution: Use a 1:1 dilution of a sample and LCS. Mix well.
7.2.2 Acceptability: 70%-130%, RPD maximum 20

7.3 Method Blank

7.3.2 Use carrier from section 6.2
7.3.3 Acceptability: MB must read below RL of 0.1mg/L

Note: Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the carrier and the standard ammonia solutions should approximate that of the samples.

7.4 Calibration Standard:

7.4.1 Stock Ammonia Standard:
7.4.1.1 Dehydrate Ammonium Chloride (NH_4Cl) in a 105°C oven.
7.4.1.2 Allow to cool in a dessicator. Weigh out 3.819 g NH4Cl.
7.4.1.3 Dilute to 1 liter with nanopure water in a volumetric flask.
7.4.1.4 Pour the solution into a 1 liter amber bottle. Keep out of sunlight.

7.4.2 Use the stock NH_3-N standard for the calibration standards (1000ppm).

7.4.3 Dilute 5 ml of stock standard to 1000 ml with preserved water. This will be the 5.0 mg/L working standard and the intermediate standard.

7.4.4 Dilute from the intermediate standard for the other working standards as follows:

7.4.4.1 2.5 mg/L standard: 50 ml of 5.0 mg/L diluted to 100 mL with preserved water.

7.4.4.2 1.0 mg/L standard: 20 mL of 5.0 mg/L diluted to 100 mL with preserved water.
7.4.4.3 0.2 mg/L standard: 4 mL of 5.0 mg/L diluted to 100 mL with preserved water.
7.4.4.4 0.05 mg/L standard: 1 mL of 5.0 mg/L diluted to 100 mL with preserved water

8.0 Procedure:

8.1 Preserve samples with H_2SO_4 to a pH of <2.

8.2 Rinse all glassware with 1:1 HCl.

8.3 Use the following volumes based on sample matrix:

8.3.1 Industrial or Influent Wastewater – 2-5mL.

8.3.2 Effluent Wastewater – 25-50 mL.

8.3.3 Well water - 50 ml.

8.3.4 Solid – Make a 1:10 water extract, extract and swirl periodically for one hour.

8.4 Dilute all samples to a final volume of 50 ml. If less than 5 ml of sample is used, dilute with carrier otherwise Nanopure water may be used.

Note: Filter all samples. Distillation is not required since computability data on representative samples is being generated to show that this step is not necessary however manual distillation will be required to resolve ant controversies (e).

8.5 Pour samples into test tubes in the test tube rack. Analyze on the lachat.

8.6 If diluted samples read below 0.1 mg/L, re-analyze using more sample and diluting to a final volume of 50 ml.

8.7 If any sample reads above 5.0 mg/L, re-analyze using less sample.

8.8 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding Nanopure water through sample line.

8.9 Arrange ammonia standards in sampler. Complete loading of sampler tray with unknown samples.

8.10 See Lachat SOP I41 for general operating instructions.

8.11 Choose method: NH4PHE

8.12 After system has stabilized with water only running through the lines and the heater temperature has reached at least 58° C, put the reagent tube into the carrier bottle.

8.13 Wait until carrier has reached the end of the board before putting the buffer tube into the reagent bottle.

8.14 Continue on in this manner, adding all of the reagents in the order in which they are numbered.

8.15 Once the baseline is stable and the temperature of the heater has returned to 58-62°C, calibration may begin.

8.16 When an acceptable calibration has been performed, submit the tray of samples.

9.0 Calculations

9.1 Prepare appropriate standard curve derived from processing ammonia standards through manifold. Compute concentration of samples by comparing sample peak areas (f) with standard curve.

9.2 Apply dilution factors to samples where less than 50ml was anlalyzed.

9.3 The reporting limit is 0.1mg/L.

9.4 Report 2 significant figures.

9.5 Inorganic Nitrogen = $NH_3N + NO_3N + NO_2N$

10.0 Definitions: See SOP Q15 – SOP Definitions

11.0 Safety: The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. A reference file of material data handling sheets is made available to all personnel involved in the chemical analysis.

See SOP S01 – Concentrated Acids and Bases
SOP S02 – Compressed Gas Cylinder Handling
SOP S03 – Spill Control Policy

12.0 Corrective Action For Out of Control Or Unacceptable Data:
See SOP Q06 – Corrective Action

13.0 Pollution Prevention and Waste Management:
See SOP S05 – Neutralization Procedure for Acid and Alkaline Wastes
SOP S06 – Disposal of Chlorinated Solvents
SOP S07 – Pollution Prevention

Method Variations

(a) Elimination of Marked Acidity or Alkalinity – Standard Methods 18th Edition 4500-NH_3 H 1b.
(b) Chlorine Pretreatment – Standard Methods 18th Edition 4500-NH_3 A 2
(c) Sample Neutralization – Standard Methods 18th Edition 4500-NH_3 A 3
(d) Reagent Recipes –Lachat Quikchem Methods NH3 Phenolate Method 10-107-06-1-B © 3/13/98 and Standard Methods 20th Edition 4500-NH_3
(e) Distillation – 40 Code of Federal Regulations part 136.
(f) Quantification Using Peak Area– Standard Methods 18th Edition 4500-NH_3 H 5

References:

Standard Methods for the Examination of Water and Wastewater APHA, AWWA, WPCF 18th Edition.

Lachat Quikchem Methods 10-107-06-2-E © 3/21/91

EPA Method 350.1 Methods for the Chemical Analysis of Waters and Wastes.

Approved by Susan K Thomas 7/10/00