Section B

PHYSICAL, INORGANIC AND MISCELLANEOUS CONSTITUENTS

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SECTION B Physical, Inorganic and Miscellaneous Constituents

Acidity, Titrimetric

Parameter

Acidity pH 8.3

Analytical Method

Auto. potentiometric titration

EMS Code

a) Automated titration **0131 X310**
b) Manual titration **0131 F044**

Introduction

Acidity of a water is its quantitative capacity to react with a strong base to a designated pH. The measurement provides an indication of corrosiveness which in turn can provide some insight into water quality.

Method Summary

The pH of the sample is determined and a measured amount of standard acid is added, as needed, to lower the pH to 4 or less. Hydrogen peroxide is added, the solution boiled for several minutes, cooled and titrated to pH 8.3 with standard base. The method measures the mineral acidity of the sample plus acidity from oxidation and hydrolysis of polyvalent cations, including salts of iron and aluminum.

MDL

Typical: 2 mg/L
Range: 2-1000 mg/L as $CaCO_3$, on a 50mL sample

Matrix

Surface and wastewaters.

Interferences and Precautions

Suspended matter present in the sample, or precipitates formed during the titration may cause sluggish electrode response. (This is overcome by allowing 15-20 second pauses between titrant additions and drop by drop titrant additions near end point). Chlorine should be neutralized with $Na_2S_2O_3$.

Sample Handling and Preservation

Plastic or glass (100mL).
Store cool, 4°C.

Stability

M. H. T.: 72 hours.

Principle or Procedure

pH meter suitable for electrometric titrations.

Precision

± 10% on sample concentrations up to 1000 mg/L.

Accuracy

None listed.

Quality Control

Cool (boiled sample) to room temperature before titrating electrometrically with standard sodium hydroxide (0.02N) to pH 8.3.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 2310 B.
b) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 305.1.

Revision History	February 14, 1994:	Publication in 1994 Laboratory Manual.
	December 31, 2000:	SEAM codes replaced by EMS codes.

Alkalinity, Phenolphthalein, Titrimetric

Parameter
Phenolphthalein alkalinity (pH 8.3)

Analytical Method
Potentiometric titration

EMS Code
a) Automated titration **0101 X310**
b) Manual titration **0101 1200**

Introduction
Alkalinity of a water is its acid-neutralizing capacity. Phenolphthalein alkalinity is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the indicator, if any, used. For a treatise on alkalinity classification and calculation of stoichiometric relationships [a].

Method Summary
An unaltered sample is titrated, using standard acid, to an electrometrically determined end point of pH 8.3. The sample must not be filtered, diluted, concentrated, or altered in any way.

MDL
Typical: 2 mg/L
Range: for all alkalinity ranges

Matrix
Drinking, surface and saline waters. Wastewaters.

Interferences and Precautions
Substances such as salts of weak organic and inorganic acids, present in large amounts, may cause interference in the electrometric pH measurements. Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

Sample Handling and Preservation
Plastic or glass (100mL).
Store cool, 4°C.

Stability
M. H. T.: 72 hours.

Principle or Procedure
pH meter or electrometric titrator.

Precision
A standard deviation of ±1 mg $CaCO_3$/L can be achieved (up to 500 mg/L).

Accuracy
None listed.

Quality Control
Standardize and calibrate pH meter according to instrument manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ± 2°C. (For <1000 mg $CaCO_3$/L use 0.02 N titrant. For >1000 mg $CaCO_3$/L use 0.1 N titrant).

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 2320 B.
b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 310.1

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Alkalinity, Total, Titrimetric, pH 4.5

Parameter

Total alkalinity pH 4.5

Analytical Method

Potentiometric Titration

EMS Code

a) Automated titration **0102 X310**
b) Manual titration **0102 1200**

Introduction

Alkalinity of a water is its acid-neutralizing capacity. It is primarily a function of carbonate, bicarbonate, and hydroxide content, although other contributing bases may be present. Alkalinity is expressed as calcium carbonate equivalent in milligrams per litre (mg $CaCO_3$/L).

Method Summary

An unaltered sample is titrated, using standard acid, to an electrometrically determined end point of pH 4.5. The sample must not be filtered, diluted, concentrated, or altered in any way.

MDL

Typical: 2 mg/L
Range: for all alkalinity ranges

Matrix

Drinking, surface and saline waters, wastewaters.

Interferences and Precautions

Substances such as salts of weak organic and inorganic acids, present in large amounts, may cause interference in the electrometric pH measurements. Oil and grease, by coating the pH electrode, may also interfere, causing sluggish response.

Sample Handling and Preservation

Plastic or glass (100mL).
Store cool, 4°C.

Stability

M. H. T.: 72 hours.

Principle or Procedure

pH meter or electrometric titrator.

Precision

A standard deviation of ±1 mg $CaCO_3$/L can be achieved. (up to 500 mg/L).

Accuracy

None listed.

Quality Control

Standardize and calibrate pH meter according to manufacturer's instructions. If automatic temperature compensation is not provided, make titration at 25 ±2°C. (For <1000 mg $CaCO_3$/L use 0.02 N titrant. For >1000 mg $CaCO_3$/L use 0.1 N titrant).

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 2320 B.
b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 310.1

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Biomass, Gravimetric, Fixed Weight (550°C)

Parameter	Biomass, (total fixed - 550°C)
Analytical Method	Gravimetric, ignition at 550°C
EMS Code	**0462 X485**
Introduction	The biomass of aquatic biota can be estimated by various means. Direct methods include dry weight, ash-free dry weight and volume of living organisms; indirect methods include total organic carbon, adenosine triphosphate (ATP) and chlorophyll-*a* determinations. The dry weight gravimetric method has an advantage over the chlorophyll-*a* method in that the latter assumes an average ratio of chlorophyll-*a* to dry weight mass; this may not accurately represent the situation under study. The ash-free weight method has the added advantage of compensating for inorganic contribution.
Method Summary	A measured volume of sample is filtered through a 0.45 µm membrane filter or a pre-rinsed, dried and pre-weighed glass fibre filter. The filter is rinsed, removed from the filtration apparatus and dried at 105°C to constant weight, cooled in a desiccator and weighed. The residue is next ignited at 550°C for 1 hour, then cooled, rewetted to restore water of hydration of minerals, re-dried at 105°C to constant weight, cooled in a desiccator and reweighed.
MDL	4 mg/L
Matrix	Fresh and marine waters, wastewater
Interferences and Precautions	The procedure is non-specific: organic detritus will contribute to the measured weight.
Sample Handling and Preservation	Bottle: 0.5 to 4.5 L plastic, unfiltered. Preservation: none. Store frozen.
Stability	M. H. T.: 7 days.
Principle or Procedure	Aquatic biota are retained on a filter and the weight loss on ignition is attributed to the mass of biota present.
Precision	None listed.
Accuracy	None listed.
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 10200 I.
b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 405.1

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Biomass, Gravimetric, Dry Weight (105°C)

Parameter

Biomass

Analytical Method

Gravimetric, dry weight at 105°C

EMS Code

a)	units = mg/L	**0460 X313**
b)	units = mg	(EMS code to be defined on request)
c)	units = mg/m^3	(EMS code to be defined on request)

Introduction

The biomass of aquatic biota can be estimated by various means. Direct methods include dry weight, ash-free dry weight and volume of living organisms; indirect methods include total organic carbon, adenosine tri-phosphate (ATP) and chlorophyll-*a* determinations. The dry weight gravi-metric method has an advantage over the chlorophyll-*a* method in that the latter assumes an average ratio of chlorophyll-*a* to dry weight mass; this may not accurately represent the situation under study.

Method Summary

A measured volume of sample is filtered through a 0.45 µm membrane filter or a pre-rinsed dried and pre-weighed glass fibre filter. The filter is rinsed, removed from the filtration apparatus and dried at 105°C for 24 hours then cooled in a desiccator and reweighed.

MDL

4 mg/L

Matrix

Fresh and marine waters, wastewater.

Interferences and Precautions

The procedure is non-specific: silt and organic detritus will contribute to the measured weight.

Sample Handling and Preservation

Bottle: 0.5 to 4.5 L plastic or glass, unfiltered.
Preservation: none. Store frozen.

Stability

M. H. T.: 7 days.

Principle or Procedure

Aquatic biota are retained on a filter and weighed.

Precision

None listed.

Accuracy

None listed.

Quality Control

Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 10200 I.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Biomass, Volatile Weight

Parameter
Volatile Biomass

Analytical Method
Calculation of Difference in Weights at 105°C and 550°C

EMS Code

a)	units = mg	**0465 CAL9**
b)	units = mg/L	**0465 XCAL**
c)	units = mg/m^3	(EMS code to be defined on request)

Introduction
Volatile Biomass is the calculated difference between Biomass Fixed Weight (550°C) and Biomass Dry Weight (105°C).

Method Summary
Biomass, Gravimetric, Fixed Weight (550°C), and **Biomass, Gravimetric, Dry Weight (105°C)**.

MDL
4 mg/L

Matrix
Fresh and marine waters, wastewater.

Interferences and Precautions
The procedure is non-specific: silt and organic detritus will contribute to the measured weight.

Sample Handling and Preservation
Bottle: 0.5 to 4.5 L plastic or glass, unfiltered.
Preservation: none. Store frozen.

Stability
M. H. T.: 7 days.

Principle or Procedure
Aquatic biota are retained on a filter and weighed. Difference in weights at 105°C and 550°C determined.

Precision
None listed.

Accuracy
None listed.

Quality Control
Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References
a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 10200 I.

Revision History

February 14, 1994:	Although method was in use, it was not included in the 1994 Laboratory Manual.
December 31, 2000:	Initial publication.

Carbon, Total Organic, (TOC)

Parameter

Total organic carbon

Analytical Method

a) Organic carbon is connected to CO_2 which is measured by infrared detector.
b) Organic carbon is converted first to CO_2, then to methane, which is measured by flame ionization detector.

EMS Code

a) IR detection **0103 X067**
b) Flame ionization detector **0103 X314**

Introduction

Organic carbon in water and wastewater is contained in a variety of organic compounds in various oxidation states. TOC analysis is independent of the oxidative state of the carbon molecule and a more specific measurement than either COD or BOD.

Method Summary

Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. CO_2 formed can be measured by infrared (IR) detector or converted to methane (CH_4) and measured by flame ionization detector (FID).

MDL

Typical: 1.0 mg TOC/L
Range: None listed

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

Carbonate and bicarbonate can interfere and must be removed or compensated for in the calculation. This procedure is applicable only to homogeneous samples which can be injected reproducibly into the apparatus by syringe or pipette. Applies to a TOC level above 1mg/L.

Sample Handling and Preservation

Plastic or glass (25mL).
Cool, 4°C., add HCl or H_2SO_4 to pH <2.

Stability

M. H. T.: 72 hours, unpreserved.
28 days, preserved.

Principle or Procedure

Apparatus for total and dissolved organic carbon.

Precision

SD = ± 8.32mg TOC/L at 107mg TOC/L.

Accuracy

As bias, + 1.08mg/L at 107mg TOC/L.

Quality Control

Protect samples from sunlight and atmospheric oxygen. For instrument calibration, the series of standards should encompass the expected concentration range of the samples. The instrument manufacturer's instructions should be followed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 5310 B.
b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 415.1.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Total Organic Carbon (TOC / Foc) in Soil/Sediment by Combustion (PBM)

Parameters

Total Organic Carbon (TOC)
Fraction Organic Carbon (Foc)

Analytical Method

Total Organic Carbon (Automated Combustion Method)

Introduction

Organic Carbon is formed in soil by the decomposition of plant and animal residue, microorganisms and soil biota. Organic carbon has many functions that are vital to soil health such as improving the structural stability of clay soils, supporting the microorganisms that make nutrients available to plants and increasing water holding capacity.

The Organic Carbon content of a soil governs the adsorption of organic compounds to the soil, and is directly related to the mobility and retardation of organic contaminants in groundwaters moving through a soil. Organic Carbon content (TOC or Foc) can be used to predict the partitioning and bioavailability of organic contaminants when they interact with a soil or sediment.

Foc is the Fraction of Organic Carbon in a soil, which is simply its Total Organic Carbon content expressed as a decimal fraction (e.g. 1.0% TOC = 0.010 Foc).

Method Summary

A small sub-sample of a dried, ground soil sample is mixed with catalyst or accelerators and heated to high temperature (generally ≥ 1000°C) within a resistance or induction furnace in a stream of oxygen to convert all forms of Carbon into CO_2. Evolved CO_2 is most commonly detected and quantified using infrared or thermal conductivity detection.

Total Organic Carbon may be determined from the difference of Total Carbon minus Total Inorganic Carbon, or else Inorganic Carbon may be physically removed from the sample by acid treatment prior to direct measurement for TOC.

For soils, TOC / Foc is measured on the < 2 mm fraction of dried, disaggregated, and sieved soil or sediment materials.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	MDL (units)	EMS Code
Total Organic Carbon (TOC)	0.050% wt/wt	N/A
Fraction Organic Carbon (Foc)	0.00050	N/A

Matrix

Soil, sediment.

Interferences and Precautions

High levels of inorganic carbon (e.g. when fragments of mollusc shells are present in a sample) can cause problems when using the TC minus IC subtraction method, because when the majority of the carbon in a sample is inorganic, the uncertainty associated with the difference of TC minus IC becomes too great to give a useful measure for TOC. In such cases, direct measurement of TOC should be used after treatment with sulfurous acid.

High levels of inorganic carbon in a sample can be detected by adding a few drops of 3M HCl to 4-6 grams of wetted sample. Effervescence indicates the presence of inorganic carbon.

Sample Handling and Preservation

Collect samples in a clean polyethylene or glass container. Glass soil jars or polyethylene bags are both appropriate container types.

Stability

Holding Time: Analyze within 28 days of collection (Reference: EPA SW-846 Chapter 3, Feb 2007).

Storage: Store at ≤6°C (≤10°C during shipment to the laboratory). Hold time can be extended indefinitely by drying the sample at <60ºC to less than ~3% moisture content.

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Procedure

Soils should be dried, disaggregated, and sieved to produce a < 2 mm fraction, prior to grinding. Exclude foreign materials (such as twigs or rocks) with dimensions exceeding 2 mm that cannot be disaggregated to pass through the 2 mm sieve. Soils with high peat content should be manually ground to pass through the 2 mm sieve, or directly transferred to the grinding step.

After drying and disaggregation, all soils must be ground or pulverized to a particle size appropriate for the size of sub-sample to be used, to ensure complete combustion and to ensure representative sampling. All of the < 2 mm fraction (or a representative portion of this fraction) must be finely ground and analyzed. Only the > 2 mm fraction is to be discarded. For small sub-samples, a manual or automated mortar and pestle is recommended.

Sample Amount Combusted:	**Grinding or Sieving Requirement:**
< 0.01 grams	minimum 100 mesh or 0.15 mm sieve
≥ 0.01 grams – 0.4 grams	minimum 60 mesh or 0.25 mm sieve
> 0.4 grams	minimum 30 mesh or 0.50 mm sieve

Inorganic carbon, typically in the forms of calcite or dolomite, must be removed prior to analysis or accounted for. Prior to instrumental analysis, inorganic carbon may be removed by treatment with 6% Sulfurous Acid (H_2SO_3) as described by the Canadian Society of Soil Science and Soil Science Society of America methods manuals.

Inorganic carbon content can also be determined separately, then subtracted from the total carbon result using the acetic acid, gravimetric or pressure calcimeter methods described by the Canadian Society of Soil Science and Soil Science Society of America methods manuals (see References).

Detailed instrumental procedures are not provided in this method, since they are specific to each instrument. Refer to the instrument operating manual provided by the manufacturer.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 replicates of one or more soil CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 90-110% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 10% relative standard deviation for soils or sediments at concentrations above ten times the MDL.

Sensitivity Requirement: A reported detection limit of 0.05% or lower must be met for this method in order to meet BC MOE requirements for Protocol 13. Qualify test results if this DL cannot be met due to analytical difficulties.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch of 20	Less than reported DL
Reference Material or Laboratory Control Sample	One per batch of 20	80 – 120%
Lab Duplicates	One per batch of 20	20% RPD

* Minimum DQOs apply at levels above 10x MDL. Report qualified data if DQOs are not met.

Method Blank: Use a carbon free <60 mesh sand matrix, e.g. silica sand muffled at > 400ºC overnight, then cooled.

Reference Material: Soil Certified Reference Materials are recommended (e.g. NIST 8704 Buffalo River Sediment, NRC Stream Sediment STSD-4). In-house Reference Materials may also be used if the target value can be demonstrated to be scientifically defensible by calibration against a soil CRM.

Laboratory Control Sample: A recommended LCS option is <60 mesh silica sand muffled at > 400ºC overnight, cooled, then spiked with known quantity of ACS grade sodium carbonate.

Prescribed Elements

The following components of this method are mandatory:

1. The < 2mm fraction of all samples must be ground to an appropriate particle size to obtain a representative, finely ground sample for analysis. Particle size requirements are dependent on size of sub-sample combusted, as defined in the procedure. (Reference: WREP 125, LECO application note 203-821-437).

2. Inorganic carbon may only be removed from the sample prior to analysis using the H_2SO_3 method. Use of other acids may result in oxidation of organic carbon (Reference: Carter).

3. For purposes of BC MOE Protocol 13, a maximum reported detection limit of 0.05% TOC (Foc 0.0005) is normally required. Data should be qualified if technical difficulties prevent this detection limit from being achieved.

4. QC requirements must be met as stated.

5. Loss on Ignition testing is not equivalent to TOC or Foc, and may not be used for purposes of BC MOE Protocol 13.

References

1. Methods of Soil Analysis: Part 3, Chemical methods, 3rd ed., ASA and SSSA, Madison, WI. Book series no. 5, pages 973-974.

2. Carter, Martin. Soil Sampling and Methods of Analysis, Ch 21, Total and Inorganic Carbon, Canadian Society of Soil Scientists (2008), pages 225-237.

3. Plant, Soil and Water Reference Methods for the Western Region, R.G. Gavlak, D.A. Hornacek and R.O. Miller. Total Organic Carbon, Combustion, Western Regional Extension Publication WREP 125, University of Alaska, Fairbanks (1994).

4. Carbon/Nitrogen in Soil and Plant Tissue, Leco Corporation application note 203-821-437, 2012.

Revision History

Aug 15, 2014	New method for BC Lab Manual in support of Protocol 13 and to improve interlaboratory consistency. Effective date of this method is Nov 1, 2014.

This protocol has been officially approved by the Director of Waste Management. It may be cited in Waste Management permits, approvals and orders, as well as legislated requirements.

Approval:_____ **Date:**_____ **Effective Date: November 1, 2014**

Chemical Oxygen Demand (COD)

Parameter

Chemical oxygen demand

Analytical Method

a) $K_2Cr_2O_7$ digestion; FAS titration (open reflux)
b) $K_2Cr_2O_7$ digestion; FAS titration (closed reflux)
c) Closed reflux, colorimetric method

EMS Code

a) Open Reflux*, FAS titration **0116 X315**
b) Closed Reflux*, FAS titration **0116 X525**
c) Closed Reflux*, colorimetric **0116 X504**
* without catalyst

(Note: similar methods, but including use of a catalyst during digestion may require new EMS codes – to be defined upon request.)

Introduction

Chemical oxygen demand (COD) is used to estimate the oxygen demand placed on a receiving water by biota in the process of assimilating the organic matter contained in a waste. For a given waste, a relationship exists between COD, BOD and TOC.

Method Summary

Organic and oxidizable inorganic substances are oxidized by potassium dichromate in H_2SO_4 solution at reflux temperature for 2 hours. Excess dichromate is titrated with standard ferrous ammonium sulfate (0.1M) using orthophenanthroline ferrous complex (ferroin) as indicator. For the colorimetric procedure, the reduced dichromate may be measured at 600 nm.

MDL

Typical: 5 mg O_2/L

Matrix

Surface water and wastewater.

Interferences and Precautions

Traces of organic material from glassware or the atmosphere may cause gross positive error. Avoid inclusion of organic materials in distilled water for reagent preparation or sample dilution.

Sample Handling and Preservation

Plastic or glass (250mL).
Store cool, 4°C., H_2SO_4 to pH <2.

Stability

M. H. T.: 28 days.

Principle or Procedure

Reflux apparatus.

Precision

SD = ± 4.15 mg O_2/L at 12.3 mg O_2/L.

Accuracy

As bias, 0.3% at 12.3 mg O_2/L.

Quality Control

None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 5220 B and Method 5220 D.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 410.2.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Clarification added regarding use of catalysts during digestion.

Chloride, Colorimetric, HgSCN

Parameter

Chloride, dissolved

Analytical Method

Automated colorimetric, mercuric thiocyanate

EMS Code

a) Filtered sample **1104 X316**
b) Unfiltered sample (will be defined upon request)

Introduction

Chloride is one of the major inorganic anions in water and wastewater. The level of chloride within a given sample may provide insight into corrosivity, taste problems, and agricultural limitations.

Method Summary

Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. Ferric nitrate reagent provides ferric ion which, with SCN, forms highly coloured ferric thiocyanate in a concentration proportional to the original chloride concentration. The instrument range of 0.5 to 50 mg/L may be extended with sample dilution.

MDL

Typical: 0.5 mg/L

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

Bromide causes positive interference.

Sample Handling and Preservation

Plastic or glass (50mL).
No preservation required.

Stability

M. H. T.: 28 days.

Principle or Procedure

Auto analyzer. 480 nm filters. 15mm tubular flow cell.

Precision

Less than 5 %.

Accuracy

None listed.

Quality Control

Where particulate matter is present, the sample must be filtered prior to the determination. Alternatively, the sample may be centrifuged or a continuous filter may be incorporated into the sample line of the automated system.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500 Cl^- E.
b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 325.2.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Chloride, Ion Chromatography

Parameter Chloride, total

Analytical Method Ion chromatography

EMS Code
a) Unfiltered **0104 X044**
b) Filtered **1104 X044**

Introduction Chloride is one of the major inorganic anions in water and wastewater. The level of chloride within a given sample may provide insight into corrosivity, taste problems, and agricultural limitations.

Method Summary A small volume of sample, typically 2 to 3mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector. While samples usually are filtered, clear solutions may be unfiltered.

MDL Typical: 0.02 mg/L

Matrix Drinking and surface waters and mixed wastewater.

Interferences and Precautions Interference can be caused by substances with retention times similar to and overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Method interference can be caused by reagent or equipment contamination.

Sample Handling and Preservation Plastic or glass (50mL). No preservation required.

Stability M. H. T.: 28 days.

Principle or Procedure Ion chromatograph. Guard, separator and suppressor columns, conductivity detector.

Precision SD = ± 0.289mg/L at 10.0 mg Cl/L (drinking water).

Accuracy Recovery = 98.2% at 10.0mg Cl/L (drinking water).

Quality Control The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing lab performance. Field and laboratory duplicates should be analyzed. Measure retention times of standards.

References
a) EPA-600/4-84-017, Test Method Technical Addition to Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), USEPA, Revised March 1983, Method 300.0
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition 1992, Method 4500 Cl-F

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Clarification note added regarding use of unfiltered samples.

Chlorine, Total Residual, Iodometric

Parameter	Residual chlorine
Analytical Method	Iodometric titration, amperometric endpoint
EMS Code	**1016 X317**
Introduction	The chlorination of water supplies and polluted waters serves primarily to destroy or deactivate disease-producing micro-organisms. Chlorine residuals are thus monitored to assess taste/odour problems and microbial destruction effectiveness.
Method Summary	Iodometric back titration is best for wastewaters but is applicable to all types of waters. (Chlorine and chloramines stoichiometrically liberate iodine from KI at pH 4 or less).
MDL	Range: None listed
Matrix	All types of waters, but especially wastewaters.
Interferences and Precautions	Manganese, iron and nitrite interference is minimized by buffering to pH 4 before adding KI. High concentrations of organics may cause uncertainty of the endpoint. Turbidity and colour make endpoint difficult to detect. Practice runs with spikes may be necessary.
Sample Handling and Preservation	Plastic or glass (200mL). No preservation required.
Stability	Analyze immediately.
Principle or Procedure	Microburet 0 - 2mL or 0 - 10mL is used. Amperometric titrator.
Precision	SD = ± 0.12mg Cl/L at 3.51mg Cl/L (river water).
Accuracy	% recovery = 107.7% at 0.84mg Cl/L (river water).
Quality Control	Use chlorine free, chlorine-demand free distilled water for dilution.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-Cl C. b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983, Method 330.2.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Total Residual Chlorine and Chloramines in Water by DPD Colorimetric – PBM

Parameter

Chlorine: total residual, free
Chloramines: total, monochloramine (NH2Cl), dichloramine (NHCl2), and nitrogen trichloride (NCl3)

Analytical Method

DPD colorimetric

Introduction

The chlorination of water supplies and polluted waters serves primarily to destroy or deactivate disease-producing micro-organisms. Chlorine applied to water in its molecular form initially forms free chlorine consisting of aqueous molecular chlorine, hypochlorous acid, and hypochlorite ion, the relative proportions of which depends on pH and temperature. Free chlorine reacts with nitrogen compounds to form combined chlorine. With ammonia, chlorine reacts to form chloramines: monochloramine, dichloramine, and nitrogen trichloride.

Method Summary

In the absence of iodide ion, free chlorine reacts with *N, N*-diethyl-*p*-phenylenediamine (DPD) to produce a red color that can be measured colorimetrically and compared to a standard curve. Subsequent addition of iodide ion acts catalytically to cause monochloramine to produce a red color. Addition of iodide to excess evokes rapid response from dichloramine. In the presence of iodide ion, nitrogen trichoride is included with dichloramine and part with free chlorine. A supplementary procedure based on adding iodide prior to DPD permits estimating the proportion of nitrogen trichloride appearing with free chlorine.

In practice, free chlorine and total chlorine can be measured using portable colorimetric field kits (i.e. HACH or equivalent). Total chlorine analysis may be used as a screen to preclude the presence of chloramines.

MDL and EMS Codes

Typical: 0.2 mg Cl_2/L
Range: up to 4.0 mg Cl_2/L

Matrix

Natural and treated waters.

Interferences and Precautions

a) The most significant interfering substance likely to be encountered in water is oxidized manganese. To correct for this, conduct analysis on a sample aliquot that sodium arsenite or thioacetamide has been added. Subtract this reading from the reading obtained by the normal procedure.
b) Presence of strong oxidizing agents (bromine, chlorine dioxide, iodine, permanganate, hydrogen peroxide, and ozone) can interfere with the measurement of free chlorine.
c) Copper up to approximately 10mg/L is overcome by the addition of EDTA.
d) High concentrations of combined chlorine can break through into the free chlorine fraction measurement. If free chlorine is to be measured in the presence of more than 0.5 mg/L combined chlorine, use the thioacetamide modification.
e) Chlorine in aqueous solutions is not stable, and chlorine in weak solutions will decrease rapidly. Exposure to strong light or agitation will accelerate the reduction of chlorine.
f) Ensure that chlorine-demand-free water is used for reagent preparation and dilutions.

Sample Handling and Preservation

Container: Glass, amber preferred, minimize headspace. Refer to Holding Time.

Preservation: None

Stability

Holding Time: Conduct chlorine analysis within 15 minutes of sampling.

Storage: Do not store samples to be analyzed for chlorine. Cool temperatures (4 ± 3 ºC), avoiding excessive light and agitation will minimize reduction of chlorine.

Procedure

The reference method (A) involves colorimetric wet chemistry techniques and can quantify total residual chlorine, free chlorine and each of chloramine species. This method can be time consuming and difficult to carry out under field conditions. Given that the chlorine should be measured as soon as possible after sample collection, portable chlorine test kits (B) (i.e. HACH or equivalent) that measure total residual chlorine, free chlorine and total chloramines are a quick and practical alternative. Should chloramine speciation be required, conduct the wet chemistry method (A).

A) Reference Method, Based on APHA 4500-Cl G

The reference method describes in detail, reagent preparation, apparatus, calibration procedures, analytical procedures potential interferences, calculations and other relationships that can affect chlorine and chloramine determinations. The following information is provided as general guidance.

Reagents:

- Phosphate buffer solution
- *N, N*-diethyl-*p*-phenylenediamine (DPD) solution
- Potassium Iodide (KI) crystals
- Thioacetimide solution
- Chorine-demand-free water

Apparatus:

- Spectrophotometer, 515 nm
- Test tubes, glass and/or cells with at a light path of 1 cm or longer
- Glassware as required

Calibration:

Use chlorine or potassium permanganate solutions to create a calibration curve at 515 nm that encompasses a chlorine (or equivalent) concentration range up to 4 mg/L. Refer to calibration procedures in the reference method.

Analytical Method:

The method is based on using 10 mL sample aliquots. Adjust reagent quantities proportionately for other sample volumes.

1. *Total chlorine:* Combine 0.5 mL each of buffer reagent and DPD indicator reagent. Add 100 mg of KI, then 10 mL of sample. Mix well, wait 2 minutes, then read color at 515 nm.
2. *Free chlorine:* Combine 0.5 mL each of buffer reagent and DPD indicator reagent then add 10 mL of sample and mix. If dichloramine is expected to be high, add 0.1 mL of freshly prepared KI solution (100 mg/100 mL). Read color immediately at 515 nm (Reading A).

3. *Monochloramine:* Continue by adding one small crystal (~0.1mg) of KI and mix. Read color at 515 nm immediately (Reading B).
4. *Dichloramine:* Continue by adding several crystals (~100 mg) and mix to dissolve. Let stand about 2 minutes and read color at 515 nm (Reading C).
5. *Nitrogen Trichloride:* Add a small crystal (~0.1mg) of KI to 10 mL of sample and mix. Mix 0.5 mL each of buffer reagent and DPD reagent, then combine with the sample mixture. Read the color at 515 nm immediately (Reading N).
6. *Chromate correction using thioacetamide:* Add 0.5 mL of thoacetamide solution to 100 mL of sample and mix. Combine 0.5 mL each of buffer reagent and DPD indicator reagent then add 10 mL of sample and mix. Read color immediately at 515 nm (1^{st} reading). Add several crystals (~100 mg) of KI and mix to dissolve. Wait 2 minutes and read the color at 515 nm (2^{nd} reading). Subtract the 1^{st} reading from reading A and the 2^{nd} reading from reading C for use in the calculations.

Calculations:

Reading	NCl_3 Absent	NCl_3 Present
A	Free Cl	Free Cl
B – A	NH_2Cl	NH_2Cl
C – B	$NHCl_2$	NH_2Cl + ½ NCl_3
N	-	Free Cl + ½ NCl_3
2(N – A)	-	NCl_3
C – N	-	$NHCl_2$

In the event that monochloramine is present with NCl_3, it will be included in Reading N, in which case obtain NCl_3 from 2(N-B). When reviewing the calculations, it is important to understand the following relationship:

Total Chloramines = Total Chlorine - Free Chlorine

If total chlorine is less than the specification for chloramine, it can be inferred that chloramine is less than the specification.

B) Portable Chlorine Test Kit

Free chlorine and total chlorine can be measured using portable field kits (HACH or equivalent). These generally contain a reaction vessel, DPD-based free chlorine and total chlorine reagents, and a color intensity measuring device (i.e. color wheel, spectrophotometer) calibrated to known chlorine concentrations. Some portable field kits utilize a color wheel, or a portable spectrophotometer - the latter is preferred based on better accuracy, precision and sensitivity. Follow the instruction provided by the manufacturer to determine total and free chlorine levels.

Calculations:

Portable field kits provide direct measurement of total and free chlorine in a water sample. The following equation is used to determine chloramine concentrations in water.

Total Chloramines = Total Chlorine - Free Chlorine

Total chlorine analysis may be used as a screen to preclude the presence of chloramines, i.e., if total chlorine is less than the total chloramine specification, then chloramine is also less than this specification.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 spikes must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 70-130% through repeat analysis of clean matrix spikes. Either chlorine or permanganate solutions may be employed to assess accuracy (refer to Procedure Calibration step).

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis. Precision measured as percent relative standard deviation (%RSD) must be <20% for all analytes.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	1 per batch	Less than reported DL
Method Spike	Optional	Optional
Duplicates	1 per batch	20%

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence (e.g. surrogate recoveries) demonstrates that the quality of associated sample data has not been adversely affected.

Prescribed Elements

The following components of this method are mandatory:

- Analysis shall be conducted using DPD to develop analyte color.
- Stated holding times must be observed. Data must be qualified when holding times are exceeded.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

- Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 21st Edition 2005, Method 4500-Cl G., DPD Colorimetric Method.
- Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 21st Edition 2005, Method 4500-Cl A, Introduction.

Revision History

June 12, 2006	2000 version was revised to include chloramine analysis and converted to PBM format.

Chlorophyll-a and Phaeophytin-a, UV-VIS With Lorenzen Calculations

Parameter

Chlorophyll-*a*; phaeophytin-*a*

Analytical Method

Ext, lor, vol, acid (chlorophyll-*a*)
Ext, lor, vol, acid (phaeophytin-*a*)

EMS Code

a) Chlorophyll-*a* **0143 X318**
b) Phaeophytin-*a* **0146 X319**

Introduction

Chlorophyll-*a* is used as an indicator of freshwater phytoplankton biomass. Phaeophytin-*a* is a degradation product of chlorophyll-*a* and is determined also. The chlorophyll-*a* /phaeophytin-*a* ratio is an indicator of phytoplankton physiological condition.

Method Summary

Phytoplankton are separated from the water sample by filtration on a glass fibre filter. The filters can be stored frozen if necessary. Pigments are extracted from the algae with an aqueous magnesium carbonate/acetone solution and with some form of cell disruption. The absorbance of the extract is determined before and after acidification. The acid converts chlorophyll to phaeophytin by displacing the magnesium in the porphyrin ring.

MDL

0.5 µg/L
The detection limit can vary with the volume of water filtered and the absorption cell path length. Assuming a 1 litre water sample, a 15mL extract volume, a 1 cm absorption cell and a minimum absorbance value of 0.001, a limit of 0.02 µg/L chlorophyll plus phaeophytin is reasonable.

Matrix

Fresh water, marine water and, with some calculation changes, periphyton plates.

Interferences and Precautions

a) Protect samples and extracts from light to avoid degradation of the chlorophylls.

b) Glass fibre filters are preferred since the fibres assist in breaking the cells during grinding. Membrane filters do not always dissolve completely in the acetone mixture and may also form a precipitate on acidification.

c) All glassware must be free from inorganic acids to prevent the conversion of chlorophyll-*a* to phaeophytin-*a*.

d) Organic acids are co-extracted with the chlorophyll and may acidify the extract, causing chlorophyll conversion. The aqueous portion of the acetone/water mixture is saturated with magnesium carbonate to neutralize these acids. The magnesium carbonate must be added as part of the extract mixture and not as particulate magnesium carbonate, since chlorophyll can adsorb to the particles and thus be removed from solution during centrifugation.

e) An accurate determination of chlorophyll depends on an accurate measurement of the absorbance of the extract and, using the literature value for the absorptivity of chlorophyll-*a*, calculating [b] the

concentration of chlorophyll-*a*. The bandwidth of the chlorophyll absorption peak is narrow; therefore the instrument bandwidth must also be narrow. A bandwidth of 0.5 - 2.0 nm is suitable. At a spectral bandwidth of 20 nm, the chlorophyll-*a* concentration may be underestimated by as much as 40%.

f) If no standard is available, confirm that the absorption cell or cuvette allows all the light from the spectrometer through the extract. Jacket and low volume cells, beam masks and/or focused beams can cause "beam clipping" which will prevent a true absorbance reading. If an extract standard is available, then masked cells can be used since the readings are compared to the standard.

g) Acidify carefully to a final molarity of not more than 0.003M to prevent the conversion of certain accessory pigments to species that absorb at the same wavelength as phaeophytin-*a*.

h) After acidification, there is a slight wavelength shift from 664 nm to 665 nm. Check that these are indeed the peak maxima since the wavelength accuracy of the spectrometer may be unknown.

i) Subtracting the absorbance reading at 750 nm before and after acidification will compensate for turbidity.

k) The presence of chlorophyll-*b* will cause a slight under-estimation of chlorophyll-*a* and an over-estimation of phaeopigments except in open ocean water where chlorophyll-*b* is undetectable.

l) Other than standard precautions, this method presents no hazards.

Sample Handling and Preservation

Collect at least 1 litre of sample. Preserve by:

a) Storing water samples at 4°C in the dark.

b) Centrifuging the samples and freezing the algae collected.

c) Filtering the samples through a Whatman GF/C or equivalent glass fibre filter. Remove as much water as possible from the filter to maintain the 90% acetone concentration in the extracting mixture. Fold the glass fibre filter into a larger piece of cellulose filter paper, label with pencil (not ink) and, if the pH of the water is 7 or greater, store frozen in the dark. If the pH is lower, extract as soon as possible.

Stability

Water samples stored at 4°C in the dark can be held up to 2 weeks. Filters from waters with a pH >7 can be stored frozen in the dark for up to 3 weeks.

Principle or Procedure

Most spectrophotometric methods differ only in the procedure used to break the algae cells. Tissue grinders, cell disrupters and ultrasonic baths are all documented. For method details, see references [a] and [c].

Precision

Precision is dependent upon the efficiency of extraction and varies with the different types of algae. Using sonic probe disruption, Daily, et al [d] quote a value of 100% ± 3% for the efficiency of recovery at relatively high levels of chlorophyll. Environment Canada [c] found that replicate analysis (N=20) of a sample extract initially adjusted to near the 0.001 absorbance unit (AU) detection limit provided an average reading of 0.0008 AU with a standard deviation of 0.0001 AU.

Accuracy

The accuracy of this test cannot be determined since no "standard" chlorophyll-containing algae exist. Extracts containing chlorophylls are available from EPA in Cincinnati.

Quality Control

Because of the lack of a SRM, QA/QC is limited to duplicates.

References

a) Standard Methods for the Examination of Water and Waste-water, APHA, AWWA, WEF,18th edition, 1992. Method 10200 H.
b) C.J. Lorenzen, Limnol, Oceanos., Vol. 12, p. 343, (1967).
c) Environment Canada, Conservation and Protection, Pacific and Yukon Regional Laboratory Manual, Chlorophyll-a and Phaeophytin, V2.2, (1989).
d) R.J. Daley, C.B.J. Gray, S.R. Brown, J. Fish. Res. Bd. Can., 30, p. 345 (1973).

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Colour, True, Single Wavelength - PBM

Parameter

Colour, True
Colour, True (pH 7)

Analytical Method

True Colour by Single Wavelength Spectrophotometer (450 – 465 nm)

Introduction

Colour in water results primarily from natural organic and humic matter. Humic acids selectively absorb UV blue and green wavelengths and, to a lesser degree the red and infrared region of the light spectrum. Colour also depends on factors that affect the solubility and stability of the dissolved and particulate fractions of water such as pH and temperature. Suspended particles such as colloids will also give waters an appearance of colour. Humic materials and the colour associated with them are removed from potable water supplies for both aesthetic and health reasons.

Method Summary

The platinum-cobalt method of measuring colour is given as the standard method, where the unit of colour being that produced by 1 mg/L platinum in the form of the chloroplatinate ion. True Colour is determined by filtering a sample through a 0.45 µm filter followed by comparison to platinum-cobalt standards. This comparison is determined from the light transmission characteristics of the filtered sample by means of a spectrophotometer in the region of 450 to 465 nm. This region is selected because the influence of turbidity following filtration is negligible at this wavelength.

Apparent Colour is determined without prior sample filtration (as per APHA 2120 A, only the Visual Comparison method should be used for Apparent Colour).

Colour in waters is pH dependent. Samples being tested for Colour should normally be tested concurrently for pH.

Because colour measurements are made for aesthetic reasons, pH adjustment is not normally recommended or necessary if the sample pH falls between 4 and 10. Even a small pH adjustment can change the solubility characteristic of substances and may interfere with colour measurements if particulate matter is formed. The default practice is for colour measurements to be conducted on samples as-received, without pH adjustment. If pH adjustment is required for a specific application, pH is adjusted to approximately pH 7, and colour is reported as such.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Colour, True	5 Colour Units	1052 1320
Colour, True (pH7)	5 Colour Units	n/a

Matrix

Freshwater, seawater, groundwater.

Interferences and Precautions

Turbidity is the main interference for true colour measurement. For measurements of True Colour, turbidity must be removed by filtration with a 0.45 µm filter. The colour of water is extremely pH dependent, and generally increases at higher pH. Sample pH should normally also be tested when colour measurements are taken.

For samples with extreme pH (outside pH 4 – 10), measurement of colour after adjustment to pH 7 may be more relevant (pH adjusted colour values must be reported as such).

Sample Handling and Preservation

Sample Containers: Glass or Plastic
Preservation: None

Stability

Holding Time: 3 days.
Storage: Store at ≤ 6 ˚C.

Procedure:

Prepare a Stock Platinum-cobalt standard (500 colour units):

Dissolve 0.249 g K_2PtCl_2 and 0.200 g $CoCl_2 \cdot 6H_2O$, along with 20 mL concentrated HCl in deionized water. Dilute to 200 mL in a volumetric flask. Pre-made certified reference materials are available for this test.

Prepare a set of calibration standards in the range of 0 to 500 CU. Use deionized water as the zero standard. Read absorbance for each standard within the wavelength of 450 to 465 nm. For spectrophotometers with fine wavelength adjustment, 456 nm is normally the preferred wavelength. Prepare a standard curve of CU versus absorbance. Matched spectrophotometer cells can be used where one cell is used to zero the instrument and the other to read samples.

For analysis of True Colour, filter samples through 0.45 µm filters. Read absorbance against the standard curve.

Dilute high colour samples to be within the standard curve.

If pH adjustment is required, adjust to approximately pH 7 (e.g. to within pH 6-8, using NaOH or H_2SO_4).

Refer to APHA method 2120 C. Color for further information and guidance.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 Lab Control Samples or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 100±10% or better for Lab Control Samples or certified reference materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 10% relative standard deviation for Lab Control Samples at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per batch of 20	Less than reported DL
LCS or Reference Material	One per batch of 20	85 – 115%
Lab Duplicates	One per batch of 20	20% RPD
* Minimum DQOs apply at levels above 10x MDL. Report qualified data when DQOs are not met.		

Method Blank: Required. Minimum one per batch of up to 20 samples.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection, minimum 1 per batch of up to 20 samples.

Reference Material or Lab Control Sample: Required. For LCS, use a platinum-cobalt standard at a concentration above 10x MDL.

Prescribed Elements

The following components of this method are mandatory:

1. A UV/VIS spectrophotometer with wavelength of 450–465 nm, or an autoanalyzer with a filter within this range must be used.
2. True Colour must be measured on samples that have been filtered through a suitable 0.45 µm filter.
3. This method is not appropriate for measurements of Apparent Colour. Apparent Colour must be measured on unfiltered samples by the Visual Comparison method.
4. Any samples which are pH adjusted prior to measurement of colour must be clearly reported as such.
5. All QC and calibration criteria must be met. Over-range samples must be diluted (alternatively, minimum values may be reported if this meets end-use requirements).
6. Specified Performance Requirements are mandatory.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

Refer also to the Visual Comparison method, which is another MOE approved technique for the measurement of True and Apparent Colour.

References

APHA Method 2120 C. Color (2011).

Revision History

Aug 15, 2014: Changed wavelength from 400 nm to 450-465 nm for consistency with APHA Method 2120 C. pH adjustment target changed to pH 7. Method changed to PBM format with prescribed elements and performance requirements. Effective date of this revision is Nov 1, 2014.

Dec 31, 2000: SEAM codes replaced by EMS codes. Out of print reference deleted.

1994: Publication in 1994 Laboratory Manual.

This protocol has been officially approved by the Director of Waste Management. It may be cited in Waste Management permits, approvals and orders, as well as legislated requirements.

Approval:_____ **Date:**_____ **Effective Date: November 1, 2014**

Colour, TAC (Total Absorbance)

Parameter Colour, Total Absorbance (TAC)

Analytical Method Spectrophotometric - integrated absorbance

EMS code **0024 XM14**

Purpose/Principle of Method The TAC Colour method was developed by the ministry to measure colour for a variety of water and effluents ranging from water that has colour derived from naturally occurring materials (leaves, bark, roots, humus, peat), and for highly coloured industrial effluent. The procedure was invented by Dr. M. Clark and developed by Dr. P. Horning.

Scope Spectrophotometric measurement of the colour of water and is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The TAC colour of a sample adjusted to pH 7.6 is determined by measuring the integrated absorbance of the filtered sample between 400 and 700 nm on a spectrophotometer. One unit of TAC colour may be defined as the colour produced by 2 mg/L platinum in the form of Chloroplatinate ion.

Range 2 - 50 TAC units (higher by dilution).

Detection Limit 2 TAC units.

Incremental Units Nearest whole number reported as integer to three significant figures.

Interferences Sample must be filtered to remove turbidity and possibility of bacterial degradation.

Precision Authentic samples at levels of 5 and 10 TAC units have been found to yield coefficients of variation of 2.5 and 0.74% respectively. TAC values are rounded to the nearest whole number. Values are most accurate in the range between 2 and 50 TAC units, and samples are diluted if necessary to fall within this range.

Sample Handling and Preservation Sample is collected in the field and submitted unfiltered and unpreserved. Sample should be kept at 4°C until filtered through a 0.45 um pore size filter in the laboratory. After filtration sample is stable until analysis. Minimum filtered volume required for analysis is 100 mL.

Apparatus and Materials

a) Eight 50 mL volumetric flasks.
b) One 200 uL pipetter and yellow pipette tip.
c) Volumetric pipettes of 1, 2, 3, 4, 6, 8 and 10 mL.
d) 50 mL beakers.
e) Hewlet Packard 8452A UV/VIS diode array spectrophotometer or equivalent and HP 89531A MS-DOS operating software revision A.02.00 copyright 1989.
f) A 5 cm spectrophotometric quartz cell.
g) A pH meter and standard buffers of pH 7.0, 4.0 and 10.0.
h) Magentic stir bars.

i) Pipetting device.
j) One 1 L volumetric flask.

Reagents

a) Stock TAC colour solution (250 TAC units):
Dissolve 1.246 grams potassium chloroplatinate, K_2PtCL_6 and 1.00 gram cobaltous cholride, $CoCL_2$ $6H_20$, in deionized water (DI). Slowly add 100 mL concentrated HCl and dilute to one litre with DI. *Note: Potassium chloroplatinate is toxic. Read MSDS before use. Wear a dust mask, lab coat, gloves, and safety goggles when weighing. Advise co-workers in the immediate vicinity of the risk precautions. Use fume hood when working with concentrated HCl. Read caution phrases on bottle before use. Remember to add acid to water. Store in fridge.

b) 0.1 N HCl (8.3 mL/L DI).

c) 0.1 N NaOH (4 g/L DI).

Analytical Procedures

a) Allow TAC stock solution to warm to room temperature from fridge.

b) Label beakers with appropriate sample numbers and pour approximately 30 - 40 mL of sample into corresponding beaker.

c) Adjust pH of sample to pH 7.6 (7.4 - 7.8) using 0.1N HCl or 0.1 N NaOH. If a precipitate forms, refilter using a 0.45 um filter. Limit volume of fluid used to pH adjust to no more than 10% of total volume.

d) Label the 50 mL volumetric flasks with the concentrations shown below. Prepare standards from the stock solution (250 TAC units) as outlined in the table:

Standard (TAC unit)	2	5	10	15	20	30	40	50
Stock Solution Vol (mL)	0.4	1	2	3	4	6	8	10

Pipette stock solution into flasks and bring up to volume with DI. Mix well by inverting flask several times.

e) Ready the spectrophotometer as follows:
1) Turn on the spectrophotometer first. The switch is at the left back.
2) Turn on the computer, monitor and printer.
3) From the “menu” screen select A) Biology Applications.
4) From the “Biology Applications” screen select A) HP Spectrophotometer.
5) From the “Top Level” screen select F2 Quantitation.
6) Select F1 Analytical Wavelength. Use arrow keys to select wavelength range and change it to a range of 400 to 700 nm.
7) Change F2 Reference Wavelength to a range of 702 to 750 nm.
8) Press F4 and select equation B CONC = k1*A + k0.
9) From F6 Option menu change the integration time to ten seconds and change averaging to ON.

f) Rinse the 5 cm spectrophotometer cell several times with DI. Fill cell with DI and scan by pressing F8 Scan Blank. This background blank will automatically be subtracted from the standards and the samples.

g) To set up the calibration curve, press F5 Calibration. Scan standards in increasing concentrations by pressing F1 SCAN STD. Rinse cell with a few millilitres of the standard before filling the cell, and rinse the cell two or three times between standards. When done, press F7 Evaluate to see the curve. Then press F10 Exit to see the percent error of the calibration curve. The maximum error allowed for any of the standards is ± 5%. The standards must be remade and reevaluated if the error is > 5%.

h) F10 Exit from calibration. To begin reading samples press F7 Analysis. Rinse the cell with a few millilitres of the sample and then fill cell. Place the cell in the spectrophotometer and press F1 Scan Sample. If the TAC unit value of the sample is greater than 50, dilute the sample. Note the dilution factor and account for it when calculating the results. Rinse the cell with DI between samples. Every tenth scan fill the cell with D1 and scan as though it were a sample. This is a check on technique and clarity of the cell. After reading all samples, obtain a hard copy (F9) of calibration curve and results. The results given are in TAC units calculated from the standard curve. Round off to the nearest whole number.

Quality Control

Reread 10% of samples. Values should fall within 10% of original value. Record in QC/TAC book. Reread samples if values differ > 10% between duplicates and inform supervisor.

Documentation of QC

a) Record source and lot number of calibration materials.
b) Record absorbance values for the 10 and 40 TAC unit standards and plot 2 point control chart. Values should not exceed 3 ± S.D. for run to proceed. If values exceed limits, reexamine calibration materials and inform supervisor.
c) All QC data and method will be reviewed annually.
d) Analyst signs off hard copy of printout of run.
e) Maintenance log will be kept for spectrophotometer.

Data Analysis

TAC units are derived from area under the curve from 400 - 700 nm compared to standard curve.

References

a) Clesceri, L.S., Greenberg, A.E., and Trussel, R.R. (eds.) 1989. Standard Methods for the Examination of Water and Wastewater. "Section 2120 Colour." APHA-AWWA-WCPF. 17th ed. (General reference regarding colours.)

Revision History

February 14, 1994:	Although method was in use, it was not included in the 1994 Laboratory Manual.
December 31, 2000:	Republication; SEAM codes replaced by EMS codes. Out of print references deleted.

Colour, True, Visual Comparison

Parameter

Colour, true

Analytical Method

Visual comparison method

EMS Code

a) Visual comparison to coloured solutions **0002 X321**
b) Visual comparison to glass disks **0002 X152**

Introduction

Colour in water may result from the presence of natural metallic ions, humus, peat materials, plankton, weeds, and industrial waste.

Method Summary

The sample is centrifuged or filtered to remove turbidity and colour is determined by visual comparison of the sample with known concentrations of coloured solutions. Comparison also may be made with special glass colour disks if they have been properly calibrated. The platinum-cobalt method of measuring colour is given as the standard method, the unit of colour being that produced by 1 mg/L platinum in the form of the chloroplatinate ion. The ratio of cobalt to platinum may be varied to match the hue in special cases; the proportion given below is usually satisfactory to match the colour of natural waters.

MDL

Typical: 5 colour units

Matrix

Water.

Interferences and Precautions

Even a slight turbidity causes the apparent colour to be noticeably higher than the true colour; therefore it is necessary to remove turbidity before the true colour can be approximated. The colour value of water is extremely pH-dependent, and invariably increases as the pH of the water is raised. For this reason, when reporting colour, pH is also determined.

Sample Handling and Preservation

Plastic or glass bottles.
Store cool, 4°C.

Stability

Make colour determinations within a reasonable period because biological or physical changes during storage may affect colour.

Principle or Procedure:

Apparatus

a) Hellige Aqua Tester.

Reagents

a) Stock platinum-cobalt standard (500 colour units):
Dissolve 0.249g K_2PtCl_2 and 0.200g $CoCl_2 \cdot 6H_2O$, along with 20mL concentrated HCl in deionized water. Dilute to 200mL in a volumetric flask.
b) Working platinum-cobalt standards:
a. 50 colour units: Dilute stock standard 1:9 with deionized water.
b. 10 colour units: Dilute stock standard 1:49 with deionized water.

Procedure

a) Using <u>un-shaken</u> sample, decant into the Aqua Tester, and record the value in colour units as determined visually.
Note: Some samples may require diluting.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 2120 B.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Conductivity, Specific

Parameter

Specific conductance

Analytical Method

Conductivity meter

EMS Code

a) Lab or Field (not in-situ)* **0011 X330**
b) In-Situ **0011 XM00**
*Note that Lab vs. Field is distinguished by the EMS Analytical Agency Code.

Introduction

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their mobility, valence, relative concentration, and temperature of measurement. Note that terms “specific conductivity” and “specific conductance” may be used synonymously.

Method Summary

The conductivity of a sample is measured by use of a self-contained conductivity meter. Field measurements with comparable instruments are reliable.

MDL

Typical: 1µS/cm

Matrix

Waters and wastewaters.

Interferences and Precautions

N/A

Sample Handling and Preservation

Plastic or glass (100mL). Cool, 4°C.

Stability

M. H. T.: 28 days.

Principle

Wheatstone bridge or equivalent.

Precision

SD = ± 7.55 at 100 µS/cm.

Accuracy

As bias, ± 2.0 µS/cm at 100 µmho/cm.

Quality Control

Instrument must be standardized with KCl solution before daily use. Conductivity cell must be kept clean. Make temperature corrections, and report result at 25°C, if sample is not analyzed at 25°C.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 2510 B.
b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 120.1.

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes. Units changed to SI. Also clarifications note added regarding conductivity vs. conductance.

Cyanate, Ion Chromatography

Parameter Cyanate

Analytical Method Ion chromatographic analysis

EMS Code Filtered sample **CYAN X044**

Introduction Cyanate (OCN^-) is a product of the alkaline chlorination process used to destroy cyanide and may be present in industrial waste streams. Cyanate is unstable at neutral or low pH.

Method Summary A small volume of sample, typically 2 to 3mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector.

MDL Typical: 0.05 mg/L
Range: 0.05 to 2.0 mg OCN/L

Matrix Fresh water and wastewaters.

Interferences and Precautions Interference can be caused by substances with retention times similar to and overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Method interference can be caused by reagent or equipment contamination. Industrial waste may contain unknown interferences.

Sample Handling and Preservation Plastic or glass (50mL). Add NaOH to pH $\geq$12.

Stability M. H. T.: 14 days.

Principle or Procedure Ion chromatograph. Guard, separator and suppressor columns, conductivity detector.

Precision None listed.

Accuracy None listed.

Quality Control The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing lab performance. Field and laboratory duplicates should be analyzed. Measure retention times of standards.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4110 B.
b) EPA-600/4-84-017, Test Method Technical Addition to Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), USEPA, Revised March 1983, Method 300.0.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Cyanide Colour Development: Isonicotinic-Barbituric Acid Method

Parameter

Cyanide; strong acid dissociable
Cyanide; weak acid dissociable

Analytical Method

Isonicotinic - barbituric acid colorimetric

EMS Code

a)	SAD Cyanide (water), units = mg/L	**0105 X323**
b)	WAD Cyanide (water), units = mg/L	**0157 X323**
c)	SAD Cyanide (soils), units = µg/g	**0105 X496**
d)	WAD Cyanide (soils), units = µg/g	**0157 X496**

Introduction

Simple cyanide may exist in solution or be liberated from complexes and collected in an alkaline trapping solution by more or less rigorous digestion/distillation procedures. This procedure allows the quantitation of the concentration of simple cyanide (NaCN), however produced, by means of a reliable, consistent colorimetric procedure.

Method Summary

An aliquot of the alkaline distillate from the analyst's choice of digestion procedure is buffered to pH<8 and reacted with chloramine-T ($CH_3C_6H_4.SO_2.N(Na)Cl.3H_2O$). Isonicotinic acid - barbituric acid solution is added and the absorbance of the solution is measured at the absorption maximum at 578 nm.

MDL

Detection limit is 0.01 mg CN/L based on the digestion of 500mL sample, 100mL of distillate trapping solution and a 10mL aliquot of trapping solution taken for colour development.

Matrix

Water (Soils and sediments can be analyzed by suspension in the digestion solution; units = µg/g).

Interferences and Precautions

Most interfering substances are removed during the distillation process. Due to the toxicity of cyanide, care should be exercised in the manipulation of cyanide-containing samples. Process in a fume cabinet or other well ventilated area. Avoid contact with or ingestion of solutions; avoid inhalation of fumes.

Sample Handling and Preservation

1L plastic bottle; add 10N NaOH to pH 12.

Stability

Preserved samples are stable indefinitely.

Principle

NaCN trapped in the alkaline distillate is buffered to pH<8 and converted to CNCl (CAUTION : CNCl is a toxic gas) by reaction with chloramine-T ($CH_3C_6H_4.SO_2.N(Na)Cl.3H_2O$). Addition of isonicotinic acid - barbituric acid solution produces a blue dye with an absorption maximum at 578 nm.

Procedure

Apparatus

a) Either a spectrophotometer or a colorimeter for use at 578 nm. An autoanalyzer with 600 nm filter and 10mm tubular flow cell may also be used.

b) Vortex mixer.

Reagents

a) Phosphate Buffer 1M:
Dissolve 138 g of sodium dihydrogen phosphate monohydrate ($NaH_2PO_4.H_2O$) in one litre of distilled water. Keep solution refrigerated.

b) Chloramine-T Solution: Prepare Daily.
Dissolve 1.0 g chloramine-T ($CH_3C_6H_4SO_2.N(Na)Cl.3H_2O$) in distilled/deionized water and dilute to 100mL.

c) Isonicotinic Acid - Barbituric Acid Solution: Prepare Daily.
In 100mL of distilled water at 60° - 70°C dissolve 1.2 g NaOH, 2.0 g isonicotinic acid and 1.0 g of barbituric acid. After cooling, carefully adjust pH to 8.5 with 1:9 acetic acid.

d) Stock Cyanide Solution (1000 ppm): This stock should be standardized once a week (see note 1).
Dissolve 1.255 g KCN (desiccated) in 0.1 N NaOH and dilute to 500mL with 0.1 N NaOH.

e) Working Cyanide Solution (1mL = 1µg CN): Prepare Daily.
Dilute 10.0mL stock (1000 ppm) cyanide solution to 100mL with 0.1N NaOH to produce the intermediate standard (100 µg/mL). Then dilute 1.00 mL of the 100 µg/mL solution to 100 mL with 0.1N NaOH to produce the working standard (1.0 µg/mL) (See note 2).

Notes:

1. Standardization of Stock CN Solution:
Titrate 10 mL stock CN solution with standard $AgNO_3$ titrant, using 0.5 mL of rhodanine indicator (20 mg p-dimethylamino-benzalrhodanine in 100 mL acetone), to a salmon pink endpoint.

$$\text{Calculation: mg CN/L} = \frac{(A-B) \times 1000}{10}$$

Where:
A = mL standard $AgNO_3$ required for stock CN solution.
B = mL standard $AgNO_3$ required for blank (0.1N NaOH).

Refer to Standard Methods, 18th ed. (1992) pg. 4-24.

2. Adjustment of Concentration:
The working cyanide solution may not be exactly 1.0 µg/mL after dilutions. Its value will depend upon the concentration of the stock CN solution, as determined by the outlined standardization procedure. Adjust the volume of stock solution taken for dilution to compensate.

Procedure

a) Preparation of Standards:
Run a full set of standards with each set of samples to be processed that day. Use 0.1N NaOH for dilution to 10 mL in a test tube.

Standard (µg)	**mL of 1.0 ppm STD**
0 . 0	0 . 0 (Reagent Blank)
0 . 5	0 . 5
1 . 0	1 . 0
2 . 0	2 . 0
3 . 0	3 . 0
4 . 0	4 . 0

b) Sample Preparation:
Sample aliquots are chosen to yield a solution containing up to 4.0 µg CN. Ideally 10 mL of the distillate should be dispensed in a test tube for colour development. If a smaller aliquot is necessary, bulk aliquot up to 10 mL with 0.1 N NaOH.

c) Colour Development:

1. Dispense 2.0 mL of phosphate buffer into the standards and samples. Always add reagents to standards first to allow for early warning if reagents are not working.

2. Add 2.0 mL chloramine-T solution to each standard and sample using an automatic pipette. Stir on vortex mixer and allow at least 2 minutes for the reaction to occur. Allow a consistent reaction time for standards and samples.

3. Add 1.0 mL of the isonicotinic acid - barbituric acid solution, stir on vortex mixer and allow colour to develop for at least 60 minutes. High concentrations may require up to two hours to develop completely.

4. Set up the calibration curve by zeroing with the reagent blank and calibrating with one of the standards (e.g. 2.0 µg). Read and record the remaining standards' absorbances and concentrations. Use a light source of 578 nm.

5. Read the concentration of each sample.

Calculations

a) For SAD- and WAD-Cyanides in water samples:

$$\mu g\ CN/mL = \frac{\mu g\ CN/aliq. \times 100\ mL}{\text{colour aliq. (mL)} \times \text{distillation aliq. (mL)}}$$

Concentration as given by spectrophotometer or colorimeter is equivalent to µg/aliq.

Detection limit is 0.01 ppm CN for a 500 mL sample, 100 mL distillation trap and a 10 mL colour aliquot.

b) For SAD- and WAD-cyanides in sediment samples:

Dry weight = Wet weight X (1-moisture fraction)

e.g., for a 5g sample with a 30% moisture content; dry weight = 5g X (1-0.3) = 3.5g.

$$\mu g\ CN/gram = \frac{\mu g\ CN/aliq. \times 100\ mL}{\text{dry wt. (g)} \times \text{colour aliq. (mL)}}$$

Detection limit is 0.30 µg/g CN for ~ 15 g sample distilled into 100mL and a 10mL aliquot taken for colour development.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992.

b) See method 4500-CN for a general treatise. Section E gives the pyridine-barbituric acid colorimetric procedure which is very similar.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Cyanide; Strong Acid Dissociable (Hydrochloric Acid - Hydroxylamine Hydrochloride Method)

Parameter

Cyanide; strong acid dissociable

Analytical Method

HCl-HH digestion; isonicotinic-barbituric acid colorimetric

EMS Code

a) AD cyanide (water), units = mg/L **0105 X324**
b) D cyanide (soils), units = µg/g **0105 X494**

Introduction

Cyanide-containing compounds occur throughout the environment and may be attributed to both natural and anthropogenic sources. Cyanide may be present in a variety of combinations with alkali alone (simple cyanides) and alkali with other metals (complex cyanides). Since the toxicity of cyanide to aquatic biota is related to the degree of dissociation of these complexes, analytical methods that distinguish between readily available and more stable forms of cyanide are appropriate. Strong acid dissociable cyanide is an estimation of total cyanide and includes the almost nondissociable as well as more readily dissociable complexes and simple cyanides.

Method Summary

The sample is subjected to a strong acid [hydrochloric acid - hydroxylamine hydrochloride (HCl-HH)] reflux digestion/ distillation. Hydrogen cyanide (HCN) is liberated from complex as well as simple cyanides and trapped in a weak NaOH solution. An aliquot of this solution is then analyzed by a colorimetric technique (See Cyanide Colour Development; Isonicotinic - Barbituric Acid Method.).

MDL

Typical: 0.05 mg CN/L

Matrix

Water (Soils and sediments can be analyzed by suspension in the digestion solution; units = µg/g).

Interferences

Most interfering substances are removed during the distillation process.

Precautions

Due to the toxicity of cyanide, care should be exercised in the manipulation of cyanide-containing samples. Process in a fume cabinet or other well ventilated area. Avoid contact with or ingestion of solutions; avoid inhalation of fumes.

Sample Handling and Preservation

If the sample was not preserved when taken, add NaOH to pH >10. Store at 4°C. For samples containing high levels of sulfide, treat as follows: Pour 50 mL of sample into a small beaker and add 2 mL $CdCl_2$ solution. If precipitate appears, mix and let settle. Decant and add more $CdCl_2$ until no more precipitate is formed. From the quantity of $CdCl_2$ solution required for 50 mL of sample, calculate the amount required for the whole sample and add to the sample container.

Stability

Preserved samples are stable indefinitely; however analysis within 7 days is recommended.

Procedure:

Reagents for Distillation

a) Hydrochloric acid - hydroxylamine hydrochloride reagent (HCl-HH) is prepared by dissolving 100 g $NH_2OH{\cdot}HCl$ in 400mL of distilled water and 500 mL of conc. HCl and diluting to one litre with distilled water.

b) Sulfamic acid.

c) NaOH, 0.2N.

d) $CdCl_2$ - Dissolve 15 g $CdCl_2$ in 100 mL of deionized/distilled water.

Reagents for Colorimetric Procedures

a) Phosphate Buffer 1M**:**
Dissolve 138g of sodium dihydrogen.
phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) in 1 litre of distilled water. Keep solution refrigerated.

b) Chloramine-T Solution: Prepare Daily.

Dissolve 1g Chloramine-T in distilled water and dilute to 100mL.

c) Isonicotinic acid - Barbituric Acid Reagent - Prepare Daily.

In 1000 mL of distilled water at 60° - 70°C dissolve 1.2 g NaOH, 2.0 g isonicontinic acid and 1.0 g of barbituric acid. After cooling, adjust pH to 8.5 with acetic acid.

d) Stock Cyanide Solution (1 mL = 1mg CN) - This stock solution should be standardized weekly.

Dissolve 1.8842 g NaCN in distilled water and dilute to 1000 mL. Adjust pH to at least 12 with NaOH. Standardize as follows: 1.0 mL aliquot of stock solution in 100 mL of distilled water at pH 12, add 0.5 mL of rhodamine indicator solution (20 mg p-dimethylaminobenzalrhodanine in 100 mL acetone) and titrate with standard $AgNO_3$ solution to a salmon-pink endpoint.

Note: Prepare a fresh stock solution when the concentration of the stock solution deteriorates to <900 mg/L.

e) Working Cyanide Solution (1mL = 1µg CN) - Prepare Daily.

Dilute 1 mL (multiplied by 1/strength of stock solution in mg CN/mL) of stock solution in 1000 mL 0.1N NaOH solution.

Procedure-HCl-HH Distillation

a) Turn on the reflux condenser cooling water fully and add sample make-up water (dechlorinated tap or distilled water) to the 1L boiling flask. The volume of water depends on sample aliquot to be taken (Note 1). Insert the thistle tube and rinse the diffuser with distilled water.

b) Add 50 mL of 0.2N NaOH and ~1 mL of cadmium chloride solution to the gas absorbing bottle as necessary (Note 2). Turn on the vacuum, and insert the diffuser into the gas washing bottle. Adjust the vacuum to produce an air entry rate of 1 - 2 bubbles per second.

c) Add 10 - 500 mL of sample, containing no more than 5 mg CN, to the boiling flask while under vacuum (Note 1). Add 1 scoop of sulfamic acid under vacuum.

d) Add 25 mL of HCl-HH reagent through the thistle tube.

e) Heat digestion mixture to a controlled boil and maintain for $1\frac{1}{4}$ hours. Make sure samples are boiling, but not bumping over. Cooling water flow rate should be adjusted to maintain vapour condensation within the first half of the condenser.

f) Turn off heat. After 5 minutes, add water to fill up the boiling flask. Turn up the vacuum to a maximum without creating an overflow in the gas washer.

g) Remove the gas washer and transfer contents, with rinsing, to a 100 mL graduated cylinder. Rinse the diffusing system and the cold finger and add the rinsings to the graduated cylinder and bulk to 100 mL.

h) If $CdCl_2$ was used and a precipitate or turbidity resulted, the solution should be filtered through Whatman 40 paper or be decanted after being allowed to settle.

Notes:

1. The volume of water added at this point depends on sample aliquot to be taken (total volume in the flask should be 700-800 mL prior to distillation).

2. Cadmium chloride is added to the gas washing bottles when samples are known or suspected to contain either sulphide, thiocyanate or thiosulfate.

Procedure-Colorimetric Method

a) Preparation of Standards
Run a full set of standards with each set. Use 0.1N NaOH for dilution.

Standard (µg)	**mL of 1.0 ppm STD**
0 . 0	0 . 0 (Reagent Blank)
0 . 2	0 . 2
1 . 0	1 . 0
2 . 0	2 . 0
3 . 0	3 . 0
4 . 0	4 . 0

b) Preparation of Samples
Sample aliquots are chosen to yield a solution containing up to 4.0 µg CN^-.

c) Colour Development

1) Dispense 10.0mL each of standards and samples into 20mm x 150mm disposable test tubes.

2) Add 2mL of phosphate buffer to standards and samples. Always add reagents to standards first to allow early warning if reagents are not working.

3) Add 0.2mL Chloramine-T solution using an automatic pipette. Stir on vortex mixer and allow at least 2.0 minutes for the reaction to occur.

4) Add 1.0mL of the isonicotinic acid - barbituric acid solution, stir on vortex mixer, allow colour to develop for at least 60 minutes; wait up to 2 hours for high concentrations.

5) Read at 600 nm against reagent blank.

d) Calculations

$$\mu g\ CN/mL = \frac{\mu g\ CN/aliq. \times 100\ mL}{\text{colour aliq. (mL)} \times \text{distillation aliq. (mL)}}$$

Detection limit is 0.005 ppm CN for a 500 mL sample distilled into 100 mL and a 10 mL aliquot taken for colour development.

References

a) Methods for Chemical Analysis of Water and Wastewater, EPA600/4-79-020, USEPA, Revised March 1983. Method 335.2

b) Standard Methods for the Examination of Water and Wastewater, 18th Edition, 1992. Method 4500-CN E.

Neither reference is specifically for the isonicotinic acid - barbituric acid colour procedure; both methods are for the pyridine - barbituric acid colour procedure which is similar.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Cyanide in Soils by Sodium Hydroxide Extraction – Prescriptive

Parameter

Weak Acid Dissociable (WAD) Cyanide, NaOH Extractable
Strong Acid Dissociable (SAD) Cyanide, NaOH Extractable
Free Cyanide, NaOH Extractable

Analytical Method

10:1 aqueous sodium hydroxide extraction followed by appropriate analytical technique.

Introduction

Cyanide and cyanide compounds are present in soil and sediment due to both natural and anthropogenic sources. Soils represent the major potential pathway for cyanide contamination of groundwater. High concentrations of cyanide in landfill waste or industrial effluents present a hazard to both soil and groundwater.

Strong Acid Dissociable Cyanide is also commonly referred to as Total Cyanide.

Method Summary

As-received (wet) soils are tumbled a minimum of 6 hours (maximum 24 hours) with 0.05 N sodium hydroxide at a ratio of 10 parts NaOH solution to one part soil (v/w). Following extraction, pH must be ≥10. If pH falls below 10, NaOH concentration is increased and the extraction procedure is repeated (as described in the procedure).

This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Cyanide, Free	0.050 mg/kg	n/a
Cyanide, WAD	0.050 mg/kg	n/a
Cyanide, SAD	0.050 mg/kg	n/a

Matrix

Soil and sediment.

Interferences

Refer to appropriate analytical methods.

Sample Handling and Preservation

Collect samples in HDPE or glass jars with Teflon®-lined lids. Protect from light. No preservation is required.

Stability

Holding Time: 14 days as-received (Ref: US EPA SW846 Ch3 Feb 2007).

Storage

Store moist soils at ≤6°C.
Extracts may be stored at ≤6°C for up to 14 days.

Procedure

Homogenize the as-received sample prior to weighing to obtain a representative aliquot. Accurately weigh a minimum of 4.0 ± 0.1 grams (wet weight). Transfer sample to a suitable extraction vessel and add 40 mL 0.05N sodium hydroxide. *Note: Larger sample sizes may be used provided a 10:1 volume to sample weight is maintained*. Cap and shake the extraction vessel.

Extract the soil for a minimum of 6 hours (to a maximum of 24 hours) by end-over-end tumbling in a rotary extraction apparatus or by shaker table or a comparable means of mechanical extraction (rolling on-axis not permitted).

Following extraction, check the pH. Optionally, the pH may also be checked mid-way through the extraction process. If the pH is found to have dropped to <10 at any time during the extraction, increase the NaOH concentration by adding 6N NaOH in 1.0 mL increments until the pH increases to above 12 and remains above 12 for at least one minute (with shaking), then repeat the extraction process described above (i.e. continue the extraction with the same portion of sample for an additional 6-24 hours, and verify pH is ≥ 10 at completion).

Centrifuge and decant or filter the extract. Analyze the extract by a Ministry-approved analytical technique for cyanide (WAD, SAD, or Free).

Convert the results back to mg/kg cyanide on a dry weight basis based on moisture correction of the original soil.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per 20 samples, minimum one per	Less than reported DL
Laboratory Control Sample	One per 20 samples, minimum one per	80 - 120%
Matrix Spike or Reference Material	One per 20 samples, minimum one per	70 - 130%
Sample Duplicate	One per 20 samples, minimum one per	≤35% RPD
* Minimum DQOs apply at levels above 10x MDL. Report qualified data if DQOs are exceeded.		

Method Blank. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory contamination. Should be matrix-matched (same concentration of reagents as calibration and QC standards) and distilled with samples in batch.

Laboratory Control Sample. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory method accuracy without matrix effects. A separate-source standard is spiked pre-extraction with a 50/50 mixture of KCN and FeCN spiking materials onto an inert solid matrix (e.g. clean sand). KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as SAD CN.

Matrix Spike or Reference Material. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory method accuracy including matrix effects. Sample Matrix Spikes are spiked post-extraction with a 50/50 mixture of KCN and FeCN spiking materials. KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as SAD CN.

Sample Duplicate. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate sample homogeneity and laboratory method precision. Sample duplicates should replicate both the extraction procedure and the analysis.

References

1. Canadian Council of Ministers of the Environment (CCME), Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites, Volume IV: Compendium of Analytical Methods for Contaminated Sites (currently draft).
2. EPA SW846 Method 9013A "Cyanide Extraction Procedure for Solids and Oils", Revision 1, November 2004.
3. Ontario MOE-LaSB Method E3015.

Revision History	Aug 15, 2014:	New prescriptive method added to BC Lab Manual to improve inter-laboratory consistency. Effective date of this method is Nov 1, 2014.

This protocol has been officially approved by the Director of Waste Management. It may be cited in Waste Management permits, approvals and orders, as well as legislated requirements.

Approval:_____ **Date:**_____ **Effective Date: November 1, 2014**

Cyanide – Strong Acid Dissociable (SAD), H2SO4 Distillation - PBM

Parameter Cyanide – Strong acid dissociable

Analytical Method H_2SO_4 Distillation

Introduction Cyanide-containing compounds occur throughout the environment and may be attributed to both natural and anthropogenic sources. Cyanide may be present in a variety of combinations with alkali alone (simple cyanides) and with alkali and other metals (complex cyanides). Since the toxicity of cyanide to aquatic biota is related to the degree of dissociation of these complexes, analytical methods that distinguish between readily available and more stable forms of cyanide are appropriate. Strong acid dissociable cyanide is an estimation of total cyanide and includes the almost non-dissociable as well as more readily dissociable complexes and simple cyanides.

Method Summary In this procedure a strong acid (H_2SO_4) reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from both simple [$A(CN)_x$] and complex [$A\text{-}M(CN)_x$] cyanides, [where A is an alkali (Na, K, NH_4) or a metal and M is a heavy metal (Fe^{2+}, Fe^{3+}, Cd, Cu, Ni, Ag, Zn and others]. The resulting HCN gas is collected and trapped in a weak NaOH scrubbing solution. Cyanide concentration in the scrubbing solution is determined by titrimetric, colorimetric, or potentiometric procedures.

This method is performance-based. Distillation using an appropriate reflux distillation apparatus (e.g. macro or midi) is a requirement but various detection methods are permitted. Validate any apparatus being considered for use to demonstrate acceptable recovery of total cyanide before use. See performance requirements. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Strong Acid Dissociable Cyanide	0.05-0.001 mg/L	

Matrix This method describes the determination of cyanide in drinking, ground, surface, and saline waters, and domestic and industrial aqueous wastes.

Interferences and Precautions Several interferences are encountered with this method. Known interferences include sulfide, aldehydes, nitrate-nitrite, thiocyanate, thiosulfate, carbonate, glucose and other sugars, and oxidizing agents such as chlorine. Most non-volatile interferences are eliminated or reduced by distillation. Fatty acids are an interference to the titrimetric determination.

When potentially complex samples are from a source being tested for the first time, prepare sample matrix spikes by fortifying with known amounts of cyanide to test for the presence of interferences, and to verify the suitability of chosen treatments for the removal of any interferences that are identified.

Sulfides: *It is preferred that sulfide treatment be carried out before preservation, but it can be done after preservation.* Sulfides can interfere by two mechanisms:
1.) Oxidized products of sulfide rapidly convert cyanide to thiocyanate, especially at high pH (APHA). Therefore, if sulfides are present at time of NaOH

preservation, free cyanide may not be detected by the method. 2.) Hydrogen sulfide distills over with cyanide, and interferes with colorimetric, titrimetric, and electrode procedures.

Testing for sulfide can be performed by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution (pH 4). Darkening of the paper indicates presence of sulfide. If sulfide is present, add lead acetate, lead carbonate or cadmium carbonate (Note: addition of too much lead acetate can reduce pH). Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample, preferably before raising pH for stabilization. Note: If particulate metal-cyanide complexes are suspected to be present, filter solution before removing sulfide, and reconstitute by returning filtered particulates to the sample bottle after sulfide removal. Note: If sulfide removal cannot be done at time of sample collection, samples may be sent unpreserved to the laboratory for sulfide treatment within 24 hours of collection.

Lead acetate strips cannot detect sulfide at ppb levels. Cadmium chloride ($CdCl_2$) may also be added to the absorbing solution to trap residual sulfides in the distillate, to prevent interferences with the colorimetric determination.

Nitrite and Nitrate: High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation nitrate and nitrite form nitrous acid that will react with some organic compounds to form oximes. Oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid. Unless it is known that nitrate and/or nitrites are not present in a sample, add 2 g of sulfamic acid after the reflux distillation system is closed and is at the proper bubble rate.

Residual Chlorine / Oxidizing Agents: Oxidizing agents such as chlorine decompose most cyanide complexes. If residual chlorine or other oxidizing agents are suspected to be present, test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at time of collection; a blue colour indicates the need for treatment (i.e. residual chlorine > 2mg/L). If a bluish discolouration is noted, add 0.1 g sodium arsenite ($NaAsO_2$) per litre of sample and retest. Sodium thiosulfate can also be used instead of sodium arsenite. Add small portions (0.02 g/L), with re-testing after each addition. Do not add excess sodium thiosulfate. To determine chlorine < 2mg/L use a DPD colorimetric method (APHA 4500-Cl.G) and add a stoichiometric amount of sodium thiosulfate solutions (APHA 4500-Cl.B.2*d*). Note: If the diagnostic test for sulfide is positive, oxidizing compounds are not expected.

Thiocyanate: SCN^- can interfere as either a positive or negative bias depending on the conditions. SCN can be converted at high acidity in the presence of a strong oxidant to free cyanide. Conversely, a negative bias can occur when SCN is decomposed in the absence of oxidants which leads to volatile carbonyl sulfide, which is converted to suphide on absorption in an alkaline liquid. The Hydroxylamine Hydrochloride (HH) method is recommended for samples high in thiocyanate, because it breaks down less SCN^- than the H_2SO_4 distillation procedure.

Aldehydes: Aldehydes (such as formaldehyde) convert cyanide to cyanohydrin which forms nitrile during distillation. This interference is not commonly associated with the analysis of mining effluent.

Other published procedures for the removal or suppression of interferences may be employed provided they have been verified to be effective through the use of matrix spikes.

Sample Handling and Preservation

Samples should be collected in plastic or glass bottles. The volume collected should be sufficient to ensure a representative sample, to allow for replicate analysis. Shield samples from UV light.

If samples are suspected to contain residual chlorine or other oxidizing agents, they must be treated with sodium arsenite or sodium thiosulfate at time of sampling. See “Residual Chlorine / Oxidizing Agents” in interference section.

If samples are suspected to contain sulfides, treat with lead acetate, lead carbonate, or cadmium carbonate (at time of sampling, if possible), to prevent the conversion of free cyanide to thiocyanate, and to prevent distillation of hydrogen sulfide. See “Sulfides” in interference section.

If samples are suspected to contain aldehydes (above approximately 0.5 mg/L), or glucose or other sugars, add 2 mL of 3.5% ethylenediamine per 100mL of sample.

Samples must either be analyzed within 24 hours of collection, or must be preserved with sodium hydroxide to pH ≥12 and cooled to 4°C at the time of collection. Approximately 1.5 grams of NaOH per 1 litre of sample is normally sufficient to achieve pH >12 (highly buffered samples may require additional NaOH).

All specified preservation techniques are ideally performed at time of collection, but may be conducted upon receipt at the laboratory within 24 hours of sample collection.

Stability

Samples: Holding time for NaOH preserved samples is 14 days when stored at 4°C and shielded from UV light**.** Unpreserved samples must be analyzed within 24 hours.

Distillates: Ideally, distillates should be analyzed within 24 hours of distillation, but when stored at 4°C away from UV light, they may be held prior to analysis for up to 72 hours.

Procedure

Detailed reagent preparation and distillation procedures are not provided in this method, since they are specific to the reflux distillation equipment utilized. Appropriate procedures are described in EPA 335.4, APHA 4500-CN C, and within manufacturer's manuals supplied with commercial distillation systems. The procedures below are brief overviews, but include the mandatory elements of the method.

Distillation Reagents: Detailed instructions for the appropriate preparation of reagents can be found in the referenced EPA and APHA methods.

1. Sulfuric Acid, 18 N, 1+1.
2. Magnesium Chloride solution.
3. Sodium Hydroxide: Make up an appropriate NaOH solution to be used as the absorber scrubber. Because the sensitivity of the colorimetric method is pH dependent, it is important to ensure that the pH of the absorber solution from any distillation procedure is adjusted to match the pH of calibration standards.
4. Sulfamic Acid (NH_2SO_3H), crystalline.

Distillation Procedure:
Set up reflux distillation apparatus as recommended by manufacturer. Distillations should be performed in an area with adequate ventilation and fume removal systems.

1. Mix sample well by shaking prior to dispensing the appropriate amount into a distilling flask. Prepare any necessary dilutions using an appropriate sodium hydroxide solution (instead of deionized water).
2. Dispense appropriate volume of the NaOH scrubber solution into scrubber flask or tube.
3. Assemble glassware, and turn on the cooling system and vacuum. Refer to manufacturer's instructions or guidance from the EPA or APHA methods for details on reflux distillation setup.
4. Ensure the system is closed and that the bubble pattern is consistent and at the rate stated by method or manufacturer.
5. Add 2g of sulfamic acid per 500 mL of distilled sample through the air inlet tube and wash down with distilled water (use proportionately less for smaller sample sizes).
6. Add 18N H_2SO_4 at a ratio of 1:10 (acid to sample) through the air inlet tube. Rinse tube with distilled water and let the air purge mix flask contents. Optionally, add $MgCl_2$ reagent through air inlet and wash down with stream of water.
   APHA Note: The requirement to use magnesium chloride in the distillation first appeared in the 15th Edition of *Standard Methods.* Review of data demonstrates that it is not essential. Use of magnesium chloride in the distillation is left to the discretion of the laboratory.
7. Turn on the heating mantles or heater manifold. Heat samples until boiling and continue boiling for at least 1 hour.
8. After at least 1 hour of boiling, turn off the heating mantles and continue the airflow (under vacuum) for 5 minutes, allowing the samples to stop boiling before turning off the vacuum pump.
9. Transfer each distillate to a well-marked plastic bottle. If the colorimetric finish will not be conducted within 12 hours, store the distillates at 4°C. ***Distillates must be analyzed within 72 hours.***

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL. Complex cyanides such as potassium ferricyanide must be evaluated. Simple cyanides like sodium or potassium cyanide should also be evaluated.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
Ref. Material or LCS	One per batch	80 – 120% or better
Lab Duplicates	Approximately 5-10%	20% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL for Method Spikes, RMs, and Duplicates. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blanks: Required. Analyze at least one Method Blank with each sample batch. Method Blank results should be below reported detection limits, or data must be qualified.

Duplicates: Sample duplicate analyses are recommended at a frequency of 5-10%.

Reference Material or Lab Control Standard (LCS): Required. If the spike sample is prepared from a secondary source from calibration standards, it can also function as a Control Standard. Otherwise, a separate Control Standard is required. Complex cyanides such as potassium ferricyanide are preferred over simple sodium or potassium cyanides.

Laboratories should establish suitable control limits and corrective actions for all Quality Control steps. Warning and Control Limits based on a statistical process control model and in keeping with the specified Performance Requirements are recommended.

Prescribed Elements

The following components of this method are mandatory:

1. 18N H_2SO_4 distillation reagent with a ratio of 1:10 (acid to sample).

2. Boiling of sample for at least 1 hour using an appropriate vacuum purge apparatus setup (e.g. as described in the EPA or APHA methods).

3. The pH of the absorber solution from any distillation procedure must match the pH of calibration standards for the determinative method.

4. Preservation protocols must be conducted as described. Preservation to ~pH 12 with sodium hydroxide within 24 hours of sampling is mandatory.

5. Stated sample holding times must be observed. Data must be qualified where holding times are exceeded.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

1. APHA, Standard Methods for the Examination of Water and Wastewater, Method 4500-CN (1999).

2. EPA Method 335.4, Determination of Total Cyanide by Semi-Automated Colorimetry, EPA/600/R-93/100, August 1993, USEPA Office of Research and Development, Washington, D.C.

3. Csikai, N.J, Barnard, A.J., Determination of Total Cyanide in Thiocyanate-containing wastewaters, Analytical Chemistry, 55, Vol. 11, 1983.

4. ISO D2036-91, Standard Test Method for Cyanide in Water, 1991.

5. Conn, K., Cyanide Analysis in Mine Effluent, Cyanide and Gold Mining industry seminar, January 22, 1981.

Revision History

Oct 13, 2006	First version of Sulfuric Acid method for BC Lab Manual.

Cyanide – Weak Acid Dissociable (WAD), Distillation - PBM

Parameter Cyanide – Weak acid dissociable (WAD)

Analytical Method Distillation

Introduction

Cyanide-containing compounds occur throughout the environment and may be attributed to both natural and anthropogenic sources. Cyanide may be present in a variety of combinations with alkali alone (simple cyanides) and with alkali and other metals (complex cyanides). Since the toxicity of cyanide to aquatic biota is related to the degree of dissociation of these complexes, analytical methods that distinguish between readily available and more stable forms of cyanide are appropriate.

Strong acid dissociable (SAD) cyanide is an estimation of total cyanide and includes the almost non-dissociable as well as more readily dissociable complexes and simple cyanides. Weak acid dissociable (WAD) cyanide includes readily dissociable and simple cyanides. WAD cyanide is approximately equivalent to cyanide amenable to chlorination – another common method used to assess the degree of cyanide availability. WAD cyanide is a greater environmental concern than SAD cyanide due to its increased availability and toxicity in the environment.

Method Summary

In this procedure a weak acid (pH 4.5 to 6.0) reflux distillation under vacuum is combined with an air purge to liberate hydrogen cyanide (HCN) from simple [$A(CN)_x$] and more easily dissociable cyanide complexes. The acetate buffer used contains zinc salts to precipitate iron cyanide as a further assurance of the selectivity of the method.

The resulting HCN gas is collected and trapped in a weak NaOH scrubbing solution. Cyanide concentration in the scrubbing solution is determined by titrimetric, colorimetric, or potentiometric procedures.

This method is performance-based. Distillation using an appropriate reflux distillation apparatus (e.g. macro or midi) is a requirement but various detection methods are permitted. Validate any apparatus being considered for use to demonstrate acceptable recovery of weak acid dissociable cyanide before use. See performance requirements. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Weak Acid Dissociable Cyanide	0.05-0.001 mg/L	

Matrix

This method describes the determination of weak acid dissociable cyanide in drinking, ground, surface, and saline waters, and domestic and industrial aqueous wastes.

Interferences and Precautions

Several interferences are encountered with this method. Known interferences include sulfide, aldehydes, thiocyanate, thiosulfate, carbonate, glucose and other sugars, and oxidizing agents such as chlorine. Most non-volatile interferences are eliminated or reduced by distillation. Fatty acids are an interference to the titrimetric determination.

When potentially complex samples are from a source being tested for the first time, prepare sample matrix spikes by fortifying with known amounts of cyanide to test for the presence of interferences, and to verify the suitability of chosen treatments for the removal of any interferences that are identified.

Sulfides: *It is preferred that sulfide treatment be carried out before preservation, but it can be done after preservation.* Sulfides can interfere by two mechanisms: 1) Oxidized products of sulfide rapidly convert cyanide to thiocyanate, especially at high pH (APHA). Therefore, if sulfides are present at time of NaOH preservation, free cyanide may not be detected by the method. 2) Hydrogen sulfide distills over with cyanide, and interferes with colorimetric, titrimetric, and electrode procedures.

Testing for sulfide can be performed by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution (pH 4). Darkening of the paper indicates presence of sulfide. If sulfide is present, add lead acetate, lead carbonate, or cadmium carbonate (Note: addition of too much lead acetate can reduce pH). Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample, preferably before raising pH for stabilization. Note: If particulate metal-cyanide complexes are suspected to be present, filter solution before removing sulfide. And reconstitute sample by returning filtered particulates to the sample bottle after sulfide removal. Note: If sulfide removal cannot be done at time of sample collection, samples may be sent unpreserved to the laboratory for sulfide treatment within 24 hours of collection.

Lead acetate strips cannot detect sulfide at ppb levels. Cadmium chloride ($CdCl_2$) may also be added to the absorbing solution to trap residual sulfides in the distillate, to prevent interferences with the colorimetric determination.

Nitrite and Nitrate: Unlike for the measurement of SAD cyanide, nitrate and nitrite do not interfere with the measurement of WAD cyanide. Therefore the addition of sulfamic acid is not required.

Residual Chlorine / Oxidizing Agents: Oxidizing agents such as chlorine decompose most cyanide complexes. If residual chlorine or other oxidizing agents are suspected to be present, test a drop of the sample with potassium iodide-starch paper (KI-starch paper) at time of collection; a blue color indicates the need for treatment (i.e. residual chlorine > 2mg/L). If a bluish discoloration is noted, add 0.1 g sodium arsenite ($NaAsO_2$) per litre of sample and retest. Sodium thiosulfate can also be used instead of sodium arsenite. Add small portions (0.02 g/L), with re-testing after each addition. Do not add excess sodium thiosulfate. To determine chlorine < 2mg/L use a DPD colorimetric method (APHA 4500-Cl.G) and add a stoichiometric amount of sodium thiosulfate solutions (APHA 4500-Cl.B.2*d*). Note: If the diagnostic test for sulfide is positive, oxidizing compounds are not expected.

Thiocyanate: SCN^- can interfere as either a positive or negative bias depending on the conditions. SCN can be converted at high acidity in the presence of a strong oxidant to free cyanide. Conversely, a negative bias can occur when SCN is decomposed in the absence of oxidants which leads to volatile carbonyl sulfide, which is converted to suphide on absorption in an alkaline liquid.

Aldehydes: Aldehydes (such as formaldehyde) convert cyanide to cyanohydrin which forms nitrile during distillation. This interference is not commonly associated with the analysis of mining effluent.

Other published procedures for the removal or suppression of interferences may be employed provided they have been verified to be effective through the use of matrix spikes.

Sample Handling and Preservation

Samples should be collected in plastic or glass bottles. The volume collected should be sufficient to ensure a representative sample and to allow for replicate analysis. Shield samples from UV light.

If samples are suspected to contain residual chlorine or other oxidizing agents, they must be treated with sodium arsenite or sodium thiosulfate at time of sampling. See “Residual Chlorine / Oxidizing Agents” in interference section.

If samples are suspected to contain sulfides, treat with lead acetate, lead carbonate, or cadmium carbonate (at time of sampling, if possible), to prevent the conversion of free cyanide to thiocyanate, and to prevent distillation of hydrogen sulfide. See “Sulfides” in interference section.

If samples are suspected to contain aldehydes (above approximately 0.5 mg/L), or glucose or other sugars, add 2 mL of 3.5% ethylenediamine per 100mL of sample.

Samples must either be analyzed within 24 hours of collection, or must be preserved with sodium hydroxide to pH ≥12 and cooled to 4°C at the time of collection. Approximately 1.5 grams of NaOH per 1 litre of sample is normally sufficient to achieve pH >12 (highly buffered samples may require additional NaOH).

All specified preservation techniques are ideally performed at time of collection, but may be conducted upon receipt at the laboratory within 24 hours of sample collection.

Stability

Samples: Holding time for NaOH preserved samples is 14 days when stored at 4°C and shielded from UV light**.** Unpreserved samples must be analyzed within 24 hours.

Distillates: Ideally, distillates should be analyzed within 24 hours of distillation, but when stored at 4°C away from UV light, they may be held prior to analysis for up to 72 hours.

Procedure

Detailed reagent preparation and distillation procedures are not provided in this method, since they are specific to the reflux distillation equipment utilized. Appropriate procedures are described in EPA 335.4, APHA 4500-CN I, and within manufacturer's manuals supplied with commercial distillation systems. The procedures below are brief overviews, but include the mandatory elements of the method.

Distillation Reagents: Detailed instructions for the appropriate preparation of reagents can be found in the referenced EPA and APHA methods. The following is based on APHA:

1. Acetic Acid, 1 + 9: mix one volume of glacial acetic acid with 9 volumes of water.
2. Acetate buffer: Dissolve 410 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL water. Add glacial acetic acid to yield a solution pH of 4.5 (approximately 500 mL).
3. Zinc acetate solution, 100 g/L: Dissolve 120 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 500 mL of water and dilute to 1 L.
4. Sodium Hydroxide: Make up an appropriate NaOH solution to be used as the absorber scrubber. Because the sensitivity of the colorimetric method is pH dependent, it is important to ensure that the pH of the absorber solution from any distillation procedure is adjusted to match the pH of calibration standards.
5. Methyl red indicator.

Distillation Procedure: Set up reflux distillation apparatus as recommended by manufacturer. Distillations should be performed in an area with adequate ventilation and fume removal systems.

1. Mix sample well by shaking prior to dispensing the appropriate amount into a distilling flask. Prepare any necessary dilutions using an appropriate sodium hydroxide solution (instead of deionized water).
2. Dispense appropriate volume of the NaOH scrubber solution into scrubber flask or tube.
3. Assemble glassware, and turn on the cooling system and vacuum. Refer to manufacturer's instructions or guidance from the EPA or APHA methods for details on reflux distillation setup.
4. Ensure the system is closed and that the bubble pattern is consistent and at the rate stated by method or manufacturer.
5. Add 20 mL each of the acetate buffer and zinc acetate solution per 500 mL of sample (use proportionately less for smaller sample sizes). Add 2 to 3 drops of methyl red indicator. Rinse tube with distilled water and let the air purge mix flask contents. If the solution is not pink, add acetic acid (1+9) until pink color persists.
6. Turn on the heating mantles or heater manifold. Heat samples until boiling and continue boiling for at least 1 hour.
7. After at least 1 hour of boiling, turn off the heating mantles and continue the airflow (under vacuum) for 5 minutes, allowing the samples to stop boiling before turning off the vacuum pump.
8. Transfer each distillate to a well-marked plastic bottle. If the colorimetric finish will not be conducted within 12 hours, store the distillates at 4°C. ***Distillates must be analyzed within 72 hours.***

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed. Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 80% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL. For WAD cyanide this should consist of simple sodium or potassium cyanides.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per batch	Less than reported DL
Ref. Material or LCS	One per batch	80 – 120% or better
Lab Duplicates	Approximately 5-10%	20% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL for Method Spikes, RMs, and Duplicates. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blanks: Required. Analyze at least one Method Blank with each sample batch. Method Blank results should be below reported detection limits, or data must be qualified.

Duplicates: Sample duplicate analyses are recommended at a frequency of 5-10%.

Reference Material or Lab Control Standard (LCS): Required. If the spike sample is prepared from a secondary source from calibration standards, it can also function as a Control Standard. Otherwise, a separate Control Standard is required. For WAD cyanide this should consist of simple sodium or potassium cyanides.

Laboratories should establish suitable control limits and corrective actions for all Quality Control steps. Warning and Control Limits based on a statistical process control model, and in keeping with the specified Performance Requirements are recommended.

Prescribed Elements

The following components of this method are mandatory:

1. Distillation shall be conducted using zinc acetate + acetate buffer solution at pH 4.5 to 6.0 as indicated by methyl red indicator solution.

2. Boiling of sample for at least 1 hour using an appropriate vacuum purge apparatus setup (e.g. as described in the EPA or APHA methods or within manufacturer's instructions).

3. The pH (normality) of the absorber solution from any distillation procedure must match the pH of calibration standards for the determinative method.

4. Preservation protocols must be conducted as described. Preservation to ~pH 12 with sodium hydroxide within 24 hours of sampling is mandatory.

5. Stated sample holding times must be observed. Data must be qualified where holding times are exceeded.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

APHA, Standard Methods for the Examination of Water and Wastewater, 4500-CN (1999).

Fluoride, Ion Selective Electrode

Parameter	Fluoride
Analytical Method	Ion selective electrode
EMS Code	**1106 X143**
Introduction	The practice of fluoridation of water supplies is a contentious public health issue which has added to the importance of testing for fluoride.
Method Summary	Fluoride (F) is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve type reference electrode and a pH meter.
MDL	Typical: 0.1 mg F/L. Range: 0.1-1000 mg F/L.
Matrix	Drinking, surface and saline waters. Wastewater.
Interferences and Precautions	pH extremes interfere; sample pH should be between 5 and 9. Polyvalent cations of silicon, iron and aluminum interfere by forming complexes with fluoride. The degree of interference depends on complexing cations, concentration of fluoride and pH of sample.
Sample Handling and Preservation	Plastic bottle, no preservation required.
Stability	M. H. T.: 28 days.
Principle or Procedure	Selective ion meter with direct concentration scale for fluoride or pH meter with expanded mV scale.
Precision	SD = ± 0.03 at 0.85 mgF/L.
Accuracy	Mean = 0.84 mg/L at 0.85 mgF/L.
Quality Control	For industrial waste samples, the regular amount of buffer may not be adequate; check pH first. If highly basic (pH > 9), add 1N HCl and adjust pH to 8.3. [Electrodes must remain in the solution at least 3 minutes or until reading has stabilized (up to 5 minutes).]
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-F C. b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983, Method 340.2.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Fluoride in Soils by 5:1 Aqueous Extraction

Parameter Fluoride in Soils

Analytical Method 5:1 Aqueous Extraction followed by appropriate analytical technique.

Introduction Fluoride in soils is regulated in BC to protect cows from fluorosis, which can occur if they are exposed to fluoride in their drinking water. A 5:1 aqueous extraction process is utilized to emulate the relevant mechanism of toxicity.

Method Summary Soils are extracted with deionized water at a ratio of 5 parts water to 1 part soil. This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Fluoride	0.1 mg/kg	not available

Matrix Soil, sediment, sludge.

Interferences and Precautions Refer to appropriate determinative methods.

Sample Handling and Preservation Collect soil samples in appropriately sized HDPE containers or Ziplock bags. No preservation is necessary. Glass containers may be used if they are tested to ensure they do not cause fluoride contamination at levels above the reporting detection limit.

Stability

Holding Time: 28 days prior to analysis (Ref. 1).

Storage: Store moist soils at ≤6°C (Ref.1 states to Cool to 4°C). Dried soils may be stored at ambient temperature. Aqueous extracts may be stored at ambient temperature or under refrigeration (Ref. 2).

Procedure

Dry the soil at <60°C, and grind gently to disaggregate (do not pulverize). Use a 10 mesh sieve to discard the >2mm fraction. Alternatively, samples may be wet-sieved.

Accurately weigh a minimum of 10.0 +/- 1.0 grams (dry weight) of prepared sample into an appropriate plastic vessel (e.g. HDPE, Teflon), preferably wide-mouthed. The extraction vessel must have a volume at least double the volume of the water that will be used for the extraction. Add an accurate volume of deionized water equal to 5 times the nominal soil weight to be extracted (e.g. 50+/-1 mL for a nominal 10 gram soil sample). Extract the soil for a minimum of 2 hours by end-over-end tumbling in a rotary extraction apparatus, or by a comparable means of mechanical agitation.

Analyze the extract by an appropriate Ministry approved analytical technique for fluoride. Clarify the extract prior to analysis using filtration or centrifugation if necessary. At this time, either Ion Chromatography or a Fluoride Ion Selective Electrode may be utilized.

Convert results back to the mg/kg fluoride concentration in the dry, sieved soil. Note that for wet-sieved samples, the moisture content of the sieved sample must be used to determine the dry weight extracted (not the moisture content of the bulk sample).

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per batch	Less than reported DL
LCS or Reference Material	One per batch	80 – 120% or better
Lab Duplicates	5%	30% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Reference Material or Lab Control Sample: Required. One per batch. Post-extraction spikes are acceptable.

References

1. US EPA, 40CFR Part 136.3.
2. APHA Standard Methods, Table 1060:I, 20th edition.

Revision History

January 22, 2008	First published version. Endorsed by BCLQAAC Sept 28, 2007.

Moisture Content

Parameter	Moisture content
Analytical Method	Homogenize, gravimetric 105°C
EMS Code	**0025 X233**
Introduction	The moisture content of soils, sediments, sludge and plant tissue can vary significantly and, while the analysis is more appropriately performed on the sample 'as received', it affords a more consistent basis for interpretation of results if they are reported on a 'dry weight' basis.
Method Summary	The sample is homogenized, moisture is removed by heating and the residue is determined gravimetrically.
MDL	Typical: 0.1%
Matrix	Soil, sediment, sludge or plant tissue.
Interferences and Precautions	Any volatile component of the sample will be lost on heating and calculated as moisture.
Sample Handling and Preservation	Plastic or glass wide-mouth bottles, 'Whirl-Pak®' bags. No preservation required; samples may be stored frozen.
Stability	M. H. T.: indefinite if hard frozen.
Principle or Procedure	Gravimetric, loss of weight on heating.
Precision	None listed.
Accuracy	None listed.
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.
References	None listed.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Nitrilotriacetic Acid by Colorimetry - PBM

Parameter

Nitrilotriacetic Acid - NTA

Analytical Method

Zinc – Zincon Colorimetry

Introduction

Nitrilotriacetic acid (NTA) is used primarily in laundry detergents as a replacement for phosphates and in the treatment of boiler water to prevent accumulation of mineral scale. Concentrations in drinking water usually do not exceed a few micrograms per litre.

NTA is not metabolized in animals and is rapidly eliminated, although some may be briefly retained in bone. It is of low acute toxicity to animals, but it has been shown to produce kidney tumours in rodents following long-term exposure to high doses. IARC has placed NTA in Group 2B. It is not genotoxic, and the reported induction of tumours is believed to be due to cytotoxicity resulting from the chelation of divalent cations such as zinc and calcium in the urinary tract, leading to the development of hyperplasia and subsequently neoplasia.

Method Summary

This method is applicable to waters in the range of 0.05 – 5 mg/L NTA. It is not applicable to salt waters. In this method, zinc forms a coloured complex with 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene (Zincon) in a solution buffered to pH 9.2. When NTA is added, the Zinc – Zincon complex is broken which reduces the absorbance in proportion to the amount of NTA present.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Codes

Analyte	Approx. MDL (mg/L)	EMS Code
Nitrilotriacetic acid	0.05	

Matrix

Surface, ground and potable waters. TCLP leachates can also be analyzed. Not applicable to saline waters.

Interferences and Precautions

Cations such as calcium, magnesium, zinc, copper, iron, and manganese complex with NTA and give a negative interference. These ions must therefore be removed by batch treating samples with ion-exchange resin. At concentrations higher than expected in typical river waters, only zinc, copper, and iron were not completely removed with ion-exchange treatment.

Sample Handling and Preservation

Glass or plastic bottles minimum 250 mL. No Preservative is required.

Stability

Holding Time: 7 days.
Storage: 4 ± 2 C.

Procedure

Reagent and Standard Preparation:

Reagent water. Use deionized or distilled water.

Sodium hydroxide, 6N. Dissolve 120 g NaOH in reagent water and dilute to 500 mL.

Buffer. Dissolve 31 g boric acid and 37 g potassium chloride in 800 mL reagent water. Adjust pH to 9.2 with 6N NaOH. Dilute to 1 L.

Hydrochloric acid, 2N. Dilute 83 mL concentrated HCl to 500 mL with distilled water.

Zinc solution. Dissolve 0.44 g $ZnSO_4 \cdot 7H_2O$ in 100 mL 2N HCl and dilute to 1 L with reagent water.

Sodium hydroxide, 1N. Dissolve 4 g NaOH in reagent water and dilute to 100 mL.

Zinc – Zincon solution. Dissolve 0.0325 g Zincon (2-carboxy-2'-hydroxy-5'-sulfoformazyl benzene) in 0.5 mL of 1N NaOH. Add 75 mL of buffer. While stirring, add 3.75 mL of Zinc solution and dilute to 250 mL with reagent water.

Ion-exchange resin. Amberlite IR-120 (plus), Na^+ form (or equivalent).

Standard Preparation

Stock NTA calibration solution. Dissolve 1.000 g $N(CH_2COOH)_3$ in reagent water, add 0.1 g NaOH and make up to 1 L in a volumetric flask. 1.00 mL = 1.00 mg NTA. This stock solution may be stored for up to 2 years.

Prepare calibration standards from the stock NTA calibration solution as shown in Table 1. Pipette the amounts shown into 100 mL volumetric flasks, then dilute to volume using reagent water. These solutions must be prepared fresh for each run.

Table 1
NTA Calibration Standards

Volume of Stock Calibration Solution, **mL**	Calibration Standard Concentration **mg/L**
0.0	0.0
0.04	0.4
0.1	1.0
0.2	2.0
0.3	3.0
0.5	5.0

QC Standard stock solution. Using a different source from that used to prepare the stock calibration solution, dissolve 1.000 g $N(CH_2COOH)_3$ in reagent water and make up to 1 L in a volumetric flask. 1.00 mL = 1.00 mg NTA. This stock may be stored for up to 2 years.

QC Standard solution, 2 mg/L. Pipette 0.2 mL of the QC Standard stock solution into a 100 mL volumetric flask and dilute to volume with reagent water. Prepare fresh for each run.

Spiked Samples (Matrix Spikes). To prepare spiked samples for QC purposes, pipette 1.5 mL of a sample and 1.5 mL of the 2 .0 mg/L calibration standard into a test tube and mix thoroughly.

Sample Preparation

Filter about 50 mL of well-mixed sample through a 0.45 μm membrane filter.

Procedure

Treat standards and blank in the same manner as filtered samples.

To a 25 mL sample in a 50 mL centrifuge tube add about 2.5 g ion-exchange resin. Agitate sample for at least 15 minutes.

Filter through coarse filter paper to remove resin. Pipette 3.0 mL of filtrate into a 17 x 100 mm polypropylene test tube. Add 5.0 mL Zinc – Zincon solution by pipette.

Using a Spectrophotometer, read absorbance against reagent water at 620 nm in a 1 cm or 2 cm cell. Record the absorbances of the calibration standards as given in the run layout in Table 4. The difference between the absorbance for the calibration blank and the absorbance for the 1.0 mg/L calibration standard is used as an instrument sensitivity check. Record this reading. If the instrument sensitivity is acceptable (within limits based on historical data), continue running standards and samples according to the run layout. If the instrument sensitivity is unacceptable, stop the run and take whatever corrective action is needed to bring sensitivity within the acceptable range before proceeding with analysis.

Establish the calibration curve relating the absorbances of the calibration standards to their concentrations. A quadratic (second order) calibration should be used if the response relationship is non-linear. Because NTA breaks the coloured complex which is being measured, increasing NTA concentration causes a decrease in absorbance.

In order for the calibration curve to be acceptable, each of the high level standards must lie within 15% of the curve and the low standard within 20% (For example, using the calibration curve, the calculated concentration for the 5.0 mg/L standard must lie between 4.25 mg/L and 5.75 mg/L). If this condition is not met, the entire calibration must be rerun.

The following sequence of calibration standards, QC, and samples is recommended:

1	Cal Blank (0 μg/L)
2	Cal Std 0.4 mg/L
3	Cal Std 1.0 mg/L
4	Cal Std 2.0 mg/L
5	Cal Std 3.0 mg/L
6	Cal Std 5.0 mg/L
7	Lab Control Sample (LCS)
8	Initial Calibration Blank, ICB
9	Sample 1
10	Sample 1 Duplicate
11	Sample 1 Spiked (Matrix Spike)
12	Sample 2
13	Sample 3
.	.

. .
. .
30 Sample 20
31 QC A, Continuing Calibration Verification (CCV)
32 Continuing Calibration Blank CCB (CCB)

Calculations

Calculate sample and QC concentrations from the calibration curve using the measured absorbances. Report values in mg/L as NTA.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples. For Initial Validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations of routinely performed tests.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) of 85% to 115% or better for clean matrix spikes or certified reference materials at concentrations above ten times the MDL.

Precision Requirement: Laboratories must demonstrate method precision equal to or better than 15% relative standard deviation for a minimum of 8 clean matrix spikes at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Method Blank	One per batch	Less than reported DL
Lab Control Sample or Ref. Material	One per batch	80% to 120% or better
Lab Duplicates	Approx. 5 – 10% or one per batch	20% RPD
Matrix Spike (optional)	Approx. 5 – 10% or one per batch	70% to 130% or better
Calibration Verification (ICV)	One per batch	80% to 120%
Continuing Calibration Verification (CCV)	Every 20 samples and end of run	80% to 120%
Continuing Calibration Blank (CCB)	Every 20 samples and end of run	Less than reported MDL

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Lab Control Sample: Required. Minimum one per batch. The LCS is generally a clean matrix (water) spiked with analyte at a level above ten times MDL.

Control Standard / Initial Calibration Verification (ICV): Required. A control standard from a source separate from the calibration standard must be analyzed to monitor calibration accuracy.

Continuing Calibration Verification (CCV): Required. Calibration standards (typically a mid-point standard) must be analyzed periodically throughout the instrument run to monitor calibration drift. A control standard may serve the same purpose.

Continuing Calibration Blank (CCB): Required.

Prescribed Elements

The following components of this method are mandatory:

a) Use of the chemistry described above, including ion exchange pretreatment, is mandatory. Volumes / ratios etc. may be modified.

b) All QC and Calibration Criteria must be met.

Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

References

a) U.S. EPA Methods for Chemical Analysis of Water and Wastes, Method 430.1 (1).

Revision History

March 31, 2005	First version published in BC Lab Manual.

Nitrogen, Ammonia, Automated Berthelot Colorimetric

Parameter

Nitrogen, ammonia

Analytical Method

Automated Berthelot colorimetric method

EMS Code

1108 X326

Introduction

Ammonia is present naturally in surface and wastewaters. It is produced largely by the hydrolysis of urea and by the deamination of organic nitrogen-containing compounds.

Method Summary

Alkaline phenol and hypochlorite react with ammonia to form indophenol blue that is proportional to ammonia concentration. Sodium nitroprusside intensifies the blue colour thus formed.

MDL

Typical: 0.005 mg/L
Range: 0.005 to 2.0 mg NH_3-N/L

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

Calcium and magnesium ions may be present in concentrations sufficient to cause precipitation problems during analysis. Sample turbidity and colour may interfere with this method.

Sample Handling and Preservation

Plastic or glass (400 mL). Cool, 4°C. , H_2SO_4 to pH < 2.

Stability

M. H. T.: 72 hours, unstabilized.
28 days, stabilized.

Principle or Procedure

Autoanalyzer with spectrometer and 630-660 nm filters and 15mm or 50mm tubular flow cell. A manual version of this method may also be employed.

Precision

SD = ± 0.005 at 4 concentrations (0.43 -1.41 mg NH_3-N/L).

Accuracy

At concentrations 0.16 and 1.44, recoveries were 107% and 99% respectively.

Quality Control

All solutions must be made using ammonia-free water. When saline waters are analyzed, synthetic ocean water is used to prepare standards.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500- NH_3 H.

b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983. Method 350.1

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Nitrogen, Ammonia, Ion Selective Electrode

Parameter Nitrogen, ammonia, dissolved

Analytical Method Ion selective electrode

EMS Code **1108 X143**

Introduction Ammonia is present naturally in surface and wastewaters. It is produced largely by deamination of organic nitrogen-containing compounds and hydrolysis of urea.

Method Summary The ammonia is determined potentiometrically using an ion selective ammonia electrode. The NH_3 electrode uses a hydrophobic gas-permeable membrane to separate the sample from NH_4Cl internal solution.

MDL

Typical:	0.05 mg/L
Range:	0.05 to 1400 mg NH_3-N/L

Matrix Drinking, surface and saline waters, wastewater.

Interferences and Precautions Volatile amines act as a positive interference. Mercury interferes by forming a complex with ammonia. Thus the sample cannot be preserved with mercuric chloride.

Sample Handling and Preservation Plastic or glass (400 mL). Cool, 4°C. H_2SO_4 to pH <2.

Stability

M. H. T.:	72 hours, unstabilized.
	28 days, stabilized.

Principle or Procedure pH meter with expanded mV scale or specific ion meter.

Precision SD = ± 0.038 at 1.00 mg NH_3-N/L.

Accuracy Recoveries = 96 and 91% at 0.19 and 0.13 mg NH_3-N/L.

Quality Control Distilled water must be ammonia free. When analyzing saline waters, standards must be made up in synthetic ocean water. See EPA Method 350.1 for preparation directions.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-NH_3 G.

b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983. Method 350.3.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Nitrogen, Nitrite

Parameter	Nitrite nitrogen, dissolved
Analytical Method	Automated colorimetric. diazotization
EMS Code	**1111 X327**
Introduction	Nitrite is of concern for a number of reasons including the formation of nitrosamines under acidic conditions.
Method Summary	The diazonium compound formed by diazotization of sulfanilamide by nitrite in water under acid conditions is coupled with N-(1-naphthyl)-ethylene-diamine dihydrochloride to produce a reddish-purple colour.
MDL	Typical: 0.005 mg N/L Range: 0.005-1.0 mg NO_2-N/L
Matrix	Drinking, surface and saline waters, wastewater.
Interferences and Precautions	Highly coloured samples may give high results. Strong oxidants or reductants readily affect nitrite concentrations. High alkalinity (>600 mg/L) gives low results due to a pH shift.
Sample Handling and Preservation	Plastic or glass (50 mL). Cool, 4°C.
Stability	M. H. T.: 48 hours.
Principle or Procedure	Spectrophotometer at 540 nm with 1 cm or larger cells. An auto-analyzer may also be employed.
Precision	None listed.
Accuracy	None listed.
Quality Control	Use distilled water free of nitrite and nitrate to prepare all reagents and standards. If sample pH is >10 or total alkalinity is >600mg/L, adjust pH to 6 with 1:3 HCl. If necessary, filter sample through 0.45 µm filter using the first portion of the filtrate to rinse the filter flask.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-$N0_3$ F. b) Methods for Chemical Analysis of Water and Wastes EPA 600/4-79-020, USEPA, Revised March 1983. Method 354.1.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Nitrogen, NO3 + NO2, Automated Cadmium Reduction, Colorimetric

Parameter
Nitrogen, nitrate + nitrite

Analytical Method
Automated cadmium reduction, diazo, colorimetric

EMS Code
1109 X328

Introduction
Total oxidized nitrogen is the sum of nitrate and nitrite. Nitrite is of concern for a number of reasons including the formation of nitrosamines under acidic conditions.

Method Summary
A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. Any nitrite already present is unaffected. The nitrite is determined by diazotizing to form a highly coloured azo dye. For the determination of nitrite alone, the reduction step is eliminated and nitrate can be determined by difference.

MDL
Typical: 0.02 mg N/L
Range: 0.02 to 10.0 mg (NO_3/NO_2)-N/L

Matrix
Surface and saline waters. Wastewater.

Interferences and Precautions
Build-up of suspended matter in reduction column restricts sample flow. Low results may be found on samples with high concentrations of iron, copper or other metals, and samples with large concentrations of oil and grease will coat the surface of the cadmium.

Sample Handling and Preservation
Plastic or glass (100 mL).
Cool, 4°C; H_2SO_4 to pH < 2.

Stability
M. H. T.: 72 hours, unstabilized.
28 days, stabilized.

Principle or Procedure
Autoanalyzer with 540 nm filters and 15 or 50mm tubular flow cell. A manual version of this technique is also available.

Precision
SD = ± 0.176 mg N/L at 2.48 mg (NO_3/$N0_2$)-N/L.

Accuracy
As bias, -0.067 mg N/L at 2.48 mg (NO_3/NO_2)-N/L.

Quality Control
Caution: samples for reduction column must not be preserved with mercuric chloride. When samples to be analyzed are saline waters, synthetic ocean water should be used in the preparation of standards. (See EPA Method 350.1). The range may be extended with sample dilution.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-$N0_3$ F.

b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983. Method 353.2 (353.3 for manual procedure).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Nitrogen, NO3 + NO2, Manual Cadmium Reduction, Colorimetric

Parameter Nitrogen, nitrate + nitrite

Analytical Method Cadmium reduction, manual

EMS Code **1109 X020**

Introduction Total oxidized nitrogen is the sum of nitrate and nitrite. Nitrite is of concern for a number of reasons including the formation of nitrosamines under acidic conditions.

Method Summary A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite is determined by diazotizing to form a highly coloured azo dye.

MDL Typical: 0.02 mg N/L

Matrix Drinking, surface and saline waters, wastewater.

Interferences and Precautions Build-up of suspended matter in the reduction column restricts sample flow. Low results may be obtained on samples with high concentrations of iron, copper or other metals. Samples with large amounts of oil and grease coat the surface of the cadmium, decreasing efficiency.

Sample Handling and Preservation Plastic or glass (100 mL).
Store cool, 4°C; H_2SO_4 to pH <2.

Stability M. H. T.: 48 hours, unstabilized.
28 days, stabilized.

Principle or Procedure Spectrophotometer at 540 nm with 1 cm or longer cells.

Precision SD= ± 0.004 and 0.005 at 0.24 and 0.55 mg (NO_3/NO_2)-N/L.

Accuracy Recoveries were 100 and 102% at 0.24 and 0.55 mg (NO_3/NO_2)-N/L.

Quality Control Caution: samples for reduction must not be preserved with mercuric chloride. Carry out procedures for turbidity removal, oil and grease removal and add EDTA to eliminate high concentrations of metals interference. The range may be extended with sample dilution.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-N0$_3$-E.

b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 353.3.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Nitrogen, Nitrate, Ion Chromatography

Parameter
Nitrate nitrogen, dissolved

Analytical Method
Ion chromatography

EMS Code

a)	filtered sample	**1110 X044**
b)	unfiltered clear sample	**0110 X044**

Introduction
Nitrate generally occurs in trace quantities in surface water but may attain high levels in some groundwater. It is an essential nutrient for many photosynthetic autotrophs and thus a concern at wastewater discharge points.

Method Summary
A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector.

MDL
Typical: 0.013 mg N/L

Matrix
Drinking and surface waters, mixed wastewater.

Interferences and Precautions
Interferences can be caused by substances with retention times similar to and overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Method interference can be caused by reagent or equipment contamination.

NOTE: Results are to be reported as N.

Sample Handling and Preservation
Plastic or glass.
Store cool, 4°C.

Stability
M. H. T.: 72 hours.

Principle or Procedure
Ion chromatograph complete with guard, separator and suppressor columns and equipped with a conductivity detector.

Precision
SD = ± 0.365 mg/L at 31.0 mg NO_3-N/L (Drinking water).

Accuracy
Mean recovery = 100.7% at 31.0 mg NO_3-N/L (Drinking water).

Quality Control
The laboratory should spike and analyze a minimum of 10 % of all samples to monitor continuing lab performance. Field and laboratory duplicates should be analyzed. Measure retention times of standards. (Nitrate exhibits large changes in retention times).

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4110.

b) EPA-600/4-84-017, Test Method Technical Addition to Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), USEPA, Revised March 1983 Method 300.0.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Total and Dissolved Nitrogen (TN) by Combustion with Chemiluminescence Detection - PBM

Parameter

Total Nitrogen as N (also known as Total Bound Nitrogen, TN_b).

Analytical Method

Oxidation of bound nitrogen components by thermal combustion with quantification of nitrogen by chemiluminescence detection. This is a performance based method.

Introduction

The method is applicable to the determination of total nitrogen in water, which includes free ammonia, ammonium, nitrite, nitrate and organic compounds capable of conversion to nitrogen oxides under oxidative conditions (e.g. proteins, peptides, nucleic acids, urea). This method does not determine molecular Nitrogen (N_2).

This method is superior to classical Total Kjeldahl Nitrogen methods in that certain refractory nitrogen containing organics not included in TKN are captured here. Organic nitrogen can be determined by difference (TN minus ammonia, nitrite, and nitrate), but is subject to a high degree of uncertainty when the sum of ammonia, nitrite, and nitrate approaches the TN concentration.

Method Summary

Combustible contents of an aqueous sample are decomposed at temperatures above 700°C (with a catalyst), or above 1100°C (catalyst optional) under oxidative conditions to quantitatively convert bound nitrogen into nitrogen oxides (NO_x). The NO_x is then quantified using a chemiluminescence detector after reaction with ozone.

This method is performance-based. The method may be optimized or modified provided that specified performance requirements are met and prescribed elements are followed.

MDL and EMS Code

Analyte	Approx. MDL	EMS Code
Total Nitrogen	0.05 to 0.5 mg/L	
Total Dissolved Nitrogen	0.05 to 0.5 mg/L	

Matrix

Fresh water, wastewater, marine water, effluent.

Interferences and Precautions

Depending on the instrument used, interferences may arise from memory effects. These may occur either from samples or standard solutions with high amounts of bound nitrogen.

Potential problems may arise with samples containing high total organic carbon (TOC) concentrations. The analysis of samples containing high TOC (e.g. > 100 mg/L) will lead to low biased results for nitrogen. Samples with high TOC must be diluted to prevent this bias (or sample spikes may be conducted to verify adequate recovery).

Moisture must be removed from combustion gases prior to detection to prevent quenching of the chemiluminescence detector.

The presence of HCl preservative in samples causes decreased detector response, so the use of matrix-matched calibration standards with respect to HCl is mandatory.

Not all organic nitrogen compounds are quantitatively converted to nitrogen oxides by the oxidation procedure used (i.e. azides). Refer to Table 1 for typical combustion recovery rates of single compounds (ref. EN 12260). Method validation steps must include an evaluation of the recoveries of various nitrogen species.

Due to increasing analytical uncertainties, this method cannot accurately determine Organic Nitrogen (by difference) when the sum of ammonia, nitrate, and nitrite approaches the Total Nitrogen concentration.

Sample Handling and Preservation

When sampling, ensure that a representative sample is obtained, and that the sample is not contaminated. Refer to the BC field sampling method for further guidance.

Sample containers can be glass or plastic. 50-100mL polyethylene bottles are recommended if samples will be frozen.

Degradation of some forms of nitrogen may occur in some samples due to biological activity unless preservation steps are taken.

Samples should be cooled to 4°C or frozen as soon as possible after sampling.

If analysis cannot be completed within 72 hours, samples should either be frozen or acidified to < pH 2 with HCl.

Stability

Holding Time – Unpreserved samples must be analyzed as soon as possible, at least within 72 hours from the time of sampling. Freezing the sample extends the holding time to 14 days. Preservation with HCl to <pH 2 extends the holding time to up to a maximum of 28 days (ref: APHA), but analysis of preserved samples within 8 days is recommended.

Storage – Store at 4°C or frozen (recommended temperature –15 to –20°C).

Procedure

Detailed instrumental procedures are not provided in this method, since they are specific to each individual total nitrogen analyzer. Appropriate procedures and guidelines are described in ASTM method D 5176 – 91, European method EN 12260, German method DIN 38 409 (Part 27), or within the instrument manuals provided with the specific instrumentation used for the analysis. Some general guidelines and recommendations are summarized below.

Working standards for this method should be prepared daily. A mixture of Urea and Tris (hydroxymethyl)aminomethane (1:1 as mg/L N) is recommended as the reference standard for calibration.

Most references for this methodology recommend using an average of multiple replicate measurements for TN. This practice is recommended as a means of improving the precision of the method, and as an additional quality control measure for the prevention of memory effects.

Total Nitrogen should be reported in units of mg of Nitrogen per litre of water. If samples are filtered, results should be reported as Total Dissolved Nitrogen.

Prescribed Elements

Required elements of this method that may not be modified include the following:

Combustion temperature must equal or exceed 1100°C if no catalyst is used, or must equal or exceed 700°C if an appropriate catalyst is used.

Chemiluminescence detection is a requirement of this method.

Calibration standards must be matrix matched with samples (particularly with respect to the HCl preservative).

Samples with TOC values exceeding 100 mg/L must be diluted prior to TN analysis (or must be spiked to verify acceptable recovery).

Specified preservation options and maximum holding times are mandatory.

Samples for Total Dissolved Nitrogen must be filtered through a 0.45 μm filter prior to analysis, and prior to preservation if samples are preserved.

Requirements specified under the Quality Control section of this method are mandatory.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below. Achievement of these requirements must be demonstrated during method validation.

Accuracy

Any instrumental conditions selected must be able to achieve average recoveries of (100±15)% on clean matrix spikes of urea and nicotinic acid at concentrations above ten times the MDL. The recoveries of other more refractory nitrogen compounds (e.g. EDTA, humic acid, and selected compounds from Table 1) must be investigated during method validation in order to optimize instrument conditions, and to verify that adequate recoveries are achieved for a wider range of nitrogen compounds.

Precision

The method must generate precision equal to or better than 15% relative standard deviation for clean matrix spikes at concentrations above ten times the MDL. Using averages of multiple sample readings improves the precision of the method.

Sensitivity Requirement

None. The method must be capable of achieving MDLs that meet the data quality objectives of the intended application.

The above values do not indicate routine control limits for QC samples, which are to be established independently by each laboratory (see Quality Control section).

Quality Control Method

Method Blanks: Analyze at least one Method Blank with each sample batch. Blank results should be below reported detection limits, or data must be qualified. A transportation blank may be carried along with the samples to check for contamination during handling.

Duplicates: Sample duplicate analyses are recommended at a frequency of about 5-10%.

Spikes / Reference Materials: At least one Clean Matrix Method Spike or Reference Material must be analyzed with each batch. Recommended spike materials include nicotinic acid or urea.

Control Standard: If the spike sample is prepared from a secondary source from calibration standards, it can also function as a Control Standard. Otherwise, a separate Control Standard is required.

Laboratories should establish suitable control limits and corrective actions for all Quality Control steps.

Recovery Data

Table 1: Single Compound Recovery Rates for $TN_{(b)}$ (taken from EN 12260).

Test Substance	Recovery (%)	Test Concentration Range (mg/L)
Ammonium sulfate	95 to 100	1 to 100
Potassium nitrate	97 to 105	10 to 50
Sodium nitrate	101	not specified
Caffeine	98	not specified
Glycine	95 to 99	10
Urea	92 to 99	10
Nicotinic acid	98 to 102	not specified
Glutamic acid	97	not specified
Thiocyanates	98	not specified
Acetanilide	99	not specified
1,6-Hexanediamine	96 to 101	10 to 50
Nitrophenols	93 to 102	10 to 50
Nitroanilines	91 to 100	10 to 50
Arginine	94 to 106	10 to 50
Sodium azide	54	not specified
Benzonitrile	94 to 102	20
Potassium hexacyanoferrate(III)	99	10
Potassium hexacyanoferrate(II)	92 to 96	10
Purine	95 to 101	20
Calcium nitrate	99 to 102	10

References

ASTM D5176-91 (2003) – Total Chemically Bound Nitrogen in Water by Pyrolysis and Chemiluminescence Detection.

EN 12260 (2001) – Determination of Nitrogen – Determination of bound nitrogen (TN_b) following oxidation to nitrogen oxides.

DIN 38 409 Part 27 (1992) – Determination of Total Bound Nitrogen (H27), German Standard Methods for the examination of water, waste water, and sludge.

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Revision History

March 31, 2005: First version published in BC Lab Manual.

Total and Dissolved Nitrogen by Persulphate Oxidation - PBM

Parameter

Total Nitrogen as N

Analytical Method

Alkaline persulphate oxidation followed by colorimetry

Introduction

Total nitrogen is the sum of most inorganic and organic forms of nitrogen, with the exception of molecular nitrogen (N_2). Total nitrogen includes free ammonia, ammonium, nitrite, nitrate, and all digestible forms of organic nitrogen (e.g. proteins, peptides, nucleic acids, urea). Some refractory nitrogen containing compounds are poorly recovered. The method is superior to the classical TKN in that certain refractory nitrogen containing organics that are not included in the TKN procedure are captured here.

If ammonia, nitrate and nitrite are determined independently, organic nitrogen can be determined by difference, but is subject to a high degree of uncertainty when the sum of ammonia, nitrite, and nitrate approaches the TN concentration.

Method Summary

All digestible forms of nitrogen, both organic and inorganic, are converted to nitrate by alkaline persulphate oxidation.

Nitrate is then determined by colorimetry. The nitrate in a digested portion of the sample is quantitatively reduced to nitrite in a reductor column containing amalgamated cadmium filings. The nitrite yielded by the reduction is then determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine to form an azo dye which is measured colorimetrically at 520 nm.

This method is performance-based. Laboratories may adopt alternative options to improve performance or efficiency provided that all stated performance requirements and prescribed (mandatory) elements are met.

MDL and EMS Code

Analyte	Approx. MDL	EMS Code
Total Nitrogen	0.02 mg/L	F005
Total Dissolved Nitrogen	0.02 mg/L	

Matrix

Potable water, effluents, wastewater, groundwater, surface water.

Interferences and Precautions

If present in sufficient concentration Hg(II) and Cu(II) ions may interfere by forming complexes having absorption bands in the region of colour measurement.

Any colour associated with the sample matrix that absorbs in the 520 nm photometer range.

The persulphate digestion is not effective in water samples with high organic loading. Matrix spikes using an organic nitrogen compound should be performed on samples that are suspected or known to have high organic loading (as indicated by historical records, by analysis for TOC, or by physical properties like turbidity, odour, or colour). Dilution of samples before digestion improves recoveries. Ammonia may be run simultaneously with TN as a digestion efficiency check (detectable levels of NH_3 indicate incomplete digestion).

Due to increasing analytical uncertainties, this method cannot accurately determine Organic Nitrogen (by difference) when the sum of ammonia, nitrate, and nitrite approaches the Total Nitrogen concentration.

Sample Handling and Preservation

Glass or plastic bottles may be used.
Samples should be stored at 4°C and may be unpreserved or preserved with H_2SO_4 to pH ≤ 2.
Samples requiring total dissolved nitrogen must be filtered through a 0.45 μm filter prior to analysis and prior to preservation if samples are preserved.

Stability

Holding Time: 3 days unpreserved.
28 days preserved (ref: APHA).

Procedure

Note: If water samples have been preserved with sulphuric acid, an aliquot must be neutralized to pH 6 - 8 before the addition of the digestion solution.

10 mL samples (or 10 mL portions of diluted samples) are mixed with 5 mL of a 2% solution of potassium persulphate, $K_2S_2O_8$ in 0.3% NaOH. This reagent is reactive and is prepared fresh daily. The samples are autoclaved in sealed tubes at 100 - 110 C for 30 – 60 minutes (1 hour recommended). The digestion converts most forms of nitrogen to nitrate.

Samples are cooled and 1.0 ml of a borate buffer (1 M H_3BO_3 in 0.8% NaOH) added. Mix by inverting at least twice. Digestates are filtered if turbid.

Samples are analyzed by colorimetry. The nitrate in a digested portion of the sample is quantitatively reduced to nitrite in a reductor column containing amalgamated cadmium filings. The nitrite yielded by the reduction is then determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine to form an azo dye which is measured colorimetrically at 520 nm.

For samples suspected or known to have high organic loading, one of the following procedures must be employed:

1. Conduct sample matrix spikes using an organic nitrogen compound to verify adequate digestion efficiency. Samples with recoveries below 80% should be diluted and re-digested until recoveries are satisfactory (or data should be qualified).

2. Conduct multiple digestions and analyses using serial dilution techniques until two dilutions agree within 15% (or data should be qualified).

3. Analyze by an alternate method (e.g. TN by Combustion – Chemiluminescence).

Refer to APHA Method 4500-N C for further information and guidance.

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the performance requirements specified below.

Accuracy and Precision requirements apply to measures of long term method performance (averages and standard deviations). They do not constitute acceptance criteria for individual QC samples (see Quality Control Section). Achievement of these requirements is to be demonstrated during initial and ongoing method validation studies. For method validations, averages of at least 8 spikes or CRMs must be assessed (preferably taken from multiple analytical batches). Ongoing re-validations or performance reviews should assess QC data encompassing longer timeframes (e.g. 6 months to 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations of routine tests.

Accuracy Requirement: Any instrumental conditions selected must be able to achieve average recoveries of (100±15)% on clean matrix spikes of urea and nicotinic acid at concentrations above ten times the MDL. The recoveries of other more refractory nitrogen compounds (e.g. EDTA, humic acid, and selected compounds from Table 1) must be investigated during method validation in order to optimize digestion and analysis conditions, and to verify that adequate recoveries are achieved for a wider range of nitrogen compounds.

Precision Requirement: The method must generate precision equal to or better than 15% relative standard deviation for clean matrix spikes of organic nitrogen compounds at concentrations above ten times the MDL.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per batch	Less than reported DL
LCS or Reference Material	One per batch	85% - 115%
Matrix Spikes	Not Specified	80% - 120%
Lab Duplicates	One per batch	≤ 15% RPD

* Minimum DQOs apply to individual QC samples, not averages, and only at levels above 10x MDL. If any DQOs are exceeded at a frequency of more than ~5%, the laboratory's method should be reviewed in an attempt to improve its performance. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

Method Blank: Required. Minimum one per batch or as necessary to ensure contamination control.

Lab Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Reference Material or Lab Control Sample: Required. Glutamic acid or nicotinic acid are recommended.

Matrix Spikes: Recommended, especially for samples which may have high organic loading. Use an organic nitrogen spiking material. EDTA, nicotinic acid, or urea are recommended.

Prescribed Elements

The following components of this method are mandatory:

1. Specified Performance Requirements are mandatory.
2. All QC requirements of this method must be met.
3. The chemistry of the persulphate digestion must be conducted as described here, or as described within APHA Method 4500 - N C (i.e. reagents, digestion temperature). Alternative amounts and volumes may be used if ratios remain the same.
4. Sample handling and preservation must be conducted as described.
5. Samples known or suspected to have high organic loadings must be treated as described.
6. Apart from these limitations, and provided performance requirements are met, laboratories may introduce modifications to this method in order to improve quality or efficiency. Laboratories must disclose to their clients where modified or alternative methods are employed.

Colorimetry is specified for the determination of nitrate. Any other recognized methods such as ion chromatography are equally acceptable provided performance requirements are met.

Recovery Data

Representative single laboratory data for recovery of selected organic nitrogen compounds is indicated below.

Compound	Concentration (mg/L)	Recovery (%)	Relative Standard Deviation (%)	Number of Data Points
Glutamic Acid	1.6	97.0	1.5	14
Glutamic Acid	0.4	93.0	6.0	14
EDTA	1.5	97.2	3.3	12

References

Analysis Method:

Nitrogen – Nitrate plus nitrite, Automated Cadmium reduction, colorimetric, Revised Dec 31 2000, BC Laboratory Methods Manual.

Digestion Method:

Eaton, A, Clesceri, L.S., Greenberg, A.E., (eds.) 1998. Standard Methods for the Examination of Water and Wastewater. "Section 4500 N C." APHA-AWWA-WPCF. 20th ed.

Revision History

March 31, 2005: First version published in BC Lab Manual.

Nitrogen, Total Kjeldahl, Automated Digestion and Colorimetric

Parameter Nitrogen, total Kjeldahl (as N)

Analytical Method Automated digestion & colorimetric

EMS Code **0113 X329**

Introduction Total Kjeldahl nitrogen is defined as the sum of free ammonia and of organic nitrogen compounds, which are converted to ammonium sulfate under the conditions of digestion and represents organically bound nitrogen in the tri-negative oxidation state. It does not include all organic nitrogen compounds.

Method Summary The sample is automatically digested with a sulfuric acid solution containing a metal catalyst. Organic nitrogen is converted to ammonium sulfate.

MDL Typical: 0.05 mg N/L
Range: 0.05 to 2.0 mg N/L

Matrix Surface and saline waters.

Interferences and Precautions Iron and chromium ions tend to catalyze while copper ions tend to inhibit the indophenol colour reaction.

Sample Handling and Preservation Plastic or glass (500 mL).
Cool, 4°C. H_2SO_4 to pH < 2.

Stability M. H. T.: 72 hours, unstabilized.
28 Days, stabilized.

Principle or Procedure Autoanalyzer with 660 nm filters and 10mm tubular flow cell. Manual adaptation of this method is also acceptable.

Precision SD = ± 0.61 mg K-N/L at 2.18 mg K-N/L.

Accuracy As bias, -0.62 K-mg N/L at 2.18 mg K-N/L.

Quality Control All solutions must be made using ammonia-free water.

References

a) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 351.1.
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-NH_3 H (for the colorimetric procedure).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Nitrogen, Total Kjeldahl, Block Digestion, Automated Berthelot Colorimetric

Parameter

Nitrogen, total Kjeldahl

Analytical Method

$HgSO_4$ digestion, auto colorimetric (Berthelot method)

EMS Code

0113 X325

Introduction

Technically, TKN is the sum of ammonia and organic nitrogen and represents organically bound nitrogen in the tri-negative oxidation state. It does not include all organic nitrogen compounds.

Method Summary

The sample is heated in the presence of sulfuric acid, potassium sulfate and mercuric sulfate for 2.5 hours. The digest is cooled, diluted to 25 mL and placed on the autoanalyzer for NH_3 determination.

MDL

Typical: 0.04 mg N/L
Range: 0.04 to 20 mg N/L

Matrix

Drinking, surface and wastewaters.

Interferences and Precautions

The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides, to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as azides, nitro compounds, hydrazones, semicarbazones and some amines.

Sample Handling and Preservation

Plastic or glass (500 mL).
Store cool, 4°C, H_2SO_4 to pH <2.

Stability

M. H. T.: 72 hours, unstabilized.
28 days, stabilized.

Principle or Procedure

Block digester and automated Berthelot colour procedure for ammonia (NH_3).

Precision

None listed.

Accuracy

None listed.

Quality Control

All solutions must be made using ammonia-free water. Use Teflon boiling stones. The range may be extended with sample dilution.

References

a) Methods for Chemical Analysis of Water and Wastes, EPA-600/4 - 79-020, Revised March 1983, Method 351.2.
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-NH_3 H (for the colorimetric procedure).

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Oxygen, Dissolved (DO)

Parameter Oxygen, dissolved

Analytical Method Oxygen probe

EMS Code **0014 XM01**

Introduction Dissolved oxygen levels in waters and wastewaters impinge on various activities within the water body. This is a key test in pollution and waste treatment process control. This probe method is recommended for those samples which contain materials which interfere with the modified Winkler procedure. It is recommended for the monitoring of streams, lakes, outfalls, etc., to obtain a continuous record of DO. Dissolved oxygen probes are available from many instrument manufacturers.

Method Summary Following the manufacturer's instructions, the probe is calibrated against air or samples of known DO concentration. The samples are then measured for DO, again following all precautions recommended by the manufacturer to insure acceptable results.

MDL Typical: 1mg O_2/L

Matrix Fresh water, marine water and wastewater.

Interferences and Precautions Membrane-covered electrode systems minimize the interferences often encountered with dropping mercury or rotating platinum electrodes. The sensing element is protected by an oxygen permeable membrane, which serves as a diffusion barrier against matrix interference problems.

Sample Handling and Preservation Glass container only (both bottle and top). For sample collection from shallow depths (less than 5 ft), use an APHA type sampler. A Kemmerer type sampler is recommended for samples collected at depths >5 ft. Fill 300 mL bottle to overflowing to maintain water seal. Store cool, 4°C.

Stability M. H. T.: 30 minutes.

Principle or Procedure The diffusion current created by migration of oxygen through a permeable membrane is linearly proportional to the concentration of molecular oxygen in the sample.

Precision and Accuracy An accuracy of ± 0.1 mg DO/L and a precision of ± 0.05mg DO/L is attainable with most commercially available systems.

Quality Control Record temperature at time of sampling.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-O G.
b) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March, 1983. Method 360.1.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

pH, Electrometric

Parameter

pH

Analytical Method

Automated electrometer

EMS Code

a)	RIS probe, measurements made compensated to 25°C	**0004 X330**
b)	RIS probe, measurements made at 25 ± .5°C	**0004 XM30**
c)	LIS probe, compensated to 25°C	**0004 5065**
d)	LIS probe, measurements made at 25 ± .5°C	**0004 F072**
e)	Flow-through cell	**0004 F073**
f)	RIS probe, in-situ measurements	**0004 XMD0**
g)	RIS probe, in-situ measurements with data logger	**0004 XM15**
h)	LIS probe, in-situ measurements	**0004 F074**
i)	LIS probe, in-situ measurements with data logger	**0004 F075**

Introduction

Measurement of pH is one of the most basic tests used to assess water quality. Technically, pH is the negative logarithm of the hydrogen ion activity (concentration) which affects practically all aspects of water supply and wastewater treatment. Its measurement thus provides insight into many aspects of water quality including corrosion properties and acid-base neutralization.

Method Summary

pH is determined electrometrically using a glass electrode with a reference electrode or a combination electrode. The sample is stirred during measurement; the sample is adjusted to 25°C, unless a temperature compensating pH electrode is used. These common types of probes are regular ion strength (RIS), flow-through, and low ionic strength (LIS).

MDL

Typical: Report pH to nearest 0.1 unit
Range: pH 0.1-14

Matrix

Fresh water, marine water and wastewater.

Interferences and Precautions

Coating of the electrode with oily or particulate matter, temperature effects, and sodium errors at pH levels >10 are interferences.

Sample Handling and Preservation

Plastic or glass (25 mL). No preservation, store cool, 4°C.

Stability

Analyze immediately; M. H. T.: 72 hours.

Principle or Procedure

pH meter, laboratory or field model, magnetic stirrer and Teflon coated stirring bar.

Precision

± 0.13 pH unit at 7.3.

Accuracy

Limit of accuracy, ± 0.1 pH uni.t

Quality Control

Calibrate with standard reference buffers at a minimum of two points that bracket the expected pH of the samples and are at least 3 pH units apart. Sample temperature should be within 2°C of buffers, if automatic temperature compensation is not provided.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-H^+ B.

b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 150.1

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Definition of RIS and LIS added.

pH, Electrometric, Performance Based Method

Parameter

pH, Performance based method format (PBM**)**

Method Codes and EMS Codes

to be defined on request

Analytical Method

pH by Electrometric Measurement using Glass Electrode and pH by Electrometric Measurement using a Low Ionic Strength (LIS) Glass Electrode.

Introduction

Measuring the pH of an aqueous solution provides an indication of its acidic (pH<7) or basic (pH>7) tendency. Most natural and effluent waters range between pH 6 and pH 9, but there are notable exceptions, such as mine drainage water and unbuffered rain water. The pH value is an important water quality parameter for evaluating corrosive action and assessing water treatment practices that involve softening or disinfection procedures. It is also used to assess the extent of pollution in precipitation.

Method Summary

The glass-electrode in combination with a reference potential provided by a saturated calomel electrode is used for pH measurement. The active element of a glass electrode is a membrane of a special glass. The membrane, on immersion in a sample, forms a partition between two liquids (electrode filling solution and the sample) of differing hydrogen ion concentration and a potential is produced between the two sides of the membrane that is proportional to the difference in pH between the liquids.

Scope and Application

This method is written in a performance based method (PBM) format. A PBM includes both the mandatory and non-mandatory elements. Provided the mandatory elements are met, laboratories have the flexibility to select analytical methods, procedures and instrumentation of their preference. The most important of the mandatory elements are the data quality objectives (DQO) specified by the ministry and the criteria set out in this methodology. The laboratories have two key responsibilities. The first is to have a detailed written operating procedure documenting how the method is carried out in their laboratory. This must include the mandatory elements. The second responsibility is to annually audit their method performance to ensure the DQO are met. Laboratories should use a documented quality system conforming to ISO 17025 [g].

NOTE: The mandatory elements of this performance based method are specified in bold text.

The pH of samples should be measured using a pH meter with appropriate electrodes for the different sample types analysed. This method is applicable to all waters between the range of 0 to 14 pH units. The range will vary depending on the pH electrode of choice, instrumentation and method chosen. For measurements of extreme pH (pH > 10 or pH <1), please see Apparatus d).

Where laboratories use modifications to this method, they must prove equivalency. Indicator paper is not appropriate for measurement of sample pH.

Interferences

a) Glass electrodes are generally not subject to interference due to the presence of turbidity, colour, oxidants, and reductants in aqueous solutions.

b) Carbon dioxide in air tends to alter the pH of waters, therefore, the pH of the sample should be measured as soon as possible after the container is first opened. This effect will be increased by sample agitation, therefore sample stirring should not be excessive.

c) Some models of pH electrodes have systematic bias to very high pH samples. This is known as the alkaline error. The alkaline error is dependent on the type of electrode used.

d) High-salt samples (e.g., seawater or brines) can pose a problem due to a large and unknown liquid junction potential when the electrode system has been calibrated in 0.1M (or less) buffers; the use of suitable high-salt buffers will help to reduce this error [b].

e) *Low Ionic Strength (LIS) Samples* - measurement difficulties are sometimes encountered for high purity waters (i.e., with conductivity < 10 µ/cm). These difficulties include, slower electrode response, increased noise pickup, and drift due to CO_2 absorption [b]. Such samples require special techniques (described in Procedure d)5) to calibrate by using Low Ionic Strength (LIS) Buffers and measured by the Low Ionic Strength Probe. There is controversy in the literature versus stirring and not stirred [l,m]. In addition, it is highly recommended conductance measurements not be taken simultaneously when employing a LIS pH electrode due to the rapid flow of KCl into the sample will bias the conductance value. **Measurement of conductance when using a LIS pH probe must be done separately.**

f) Oil and grease or particulate matter may coat the pH electrode and interfere by hindering migration of electrons across the glass membrane, thus causing a sluggish response. Coatings can usually be removed by gentle wiping, detergent washing, or clean the electrode with a solvent miscible with water, (e.g., acetone and then rinse carefully with Type 1 water). Additional treatment may require cleaning with dilute HCl. Follow the manufacturer's electrode-cleaning procedures to refurbish/recondition the electrode.

Note 1: Take all precautions not to scratch the electrode surface.

g) pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes, and chemical effects caused by equilibrium changes. Choose an instrument which corrects for the change in electrode output at various temperatures**. For instruments that do not correct for chemical equilibrium effect (the change of pH inherent in the sample at various temperatures), always calibrate the electrode with pH buffers at a specified temperature and perform pH measurement at that temperature.** In addition, always record the temperature at which pH is measured. This is critical especially when taking field pH measurements, temperature correction needs to be applied if pH measuring device does not have temperature compensation capabilities (Procedure e)(Field pH Measurements).

h) Sample carry over between samples is a common problem. For very different pH samples measured with automated systems a single wash step between analyses may not be adequate. **Ensure adequate wash step(s) between sample measurements.**

i) Some cations may compete against hydrogen ion for active sites on the glass membrane of the electrode if the water sample is high in ionic strength.

Definitions

Certified Reference Material (CRM) - A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body.

Reference Material (RM) - A material or substance, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.

Duplicate - A quality control sample, often chosen randomly, from a batch of samples and undergoing separate, but identical sample preparation and analysis whose purpose is to monitor method precision and sample homogeneity.

Method Blank - A quality control sample that is free of the target parameter or analyte and contains only the reagents used and undergoes the same analysis procedure as the unknown sample. The method blank is used to monitor possible contamination sources.

pH - pH is defined to be the negative logarithm of the hydrogen ion activity:

$$pH = - \log (a_{H^+})$$

However, this definition cannot be rigorously applied in practice, because single ion activities such as a_{H^+} cannot be measured. Instead, International Union of Pure and Applied Chemistry (IUPAC) recommends the following operational definition of pH:

$$pH = pH_s \pm \frac{(E - E_s) F}{2.3026\ RT}$$

where:
- E = electromotive force (emf as volts) of a pH cell with the electrode system immersed in the sample solution.
- E_s = emf obtained when the electrode system is immersed in a reference buffer solution.
- F = Faraday constant (9.649×10^4 coulomb/mole).
- R = gas constant (8.3143 Joule / °K mole).
- T = absolute temperature, °K.
- pH_s = assigned pH of NIST reference buffer, such that pH_s represents the - log (a_H+) as nearly as possible.

Liquid junction - This potential exists between the filling solution in the reference electrode (e.g., *potential* saturated KCl) and the sample whenever these two solutions are different - it results from the inter-diffusion of ions in the two solutions. Ideally the liquid junction potential is near zero and is stable; stability is particularly important for low conductivity waters (< 100 µS/cm). Errors in pH measurement due to liquid junction potential variations are minimised by using buffers and samples at similar ionic strength (Interferences d & e).

Sample Collection and Preservation

a) Sampling must be done by qualified personnel, experienced in sampling procedures and working under standard documented operating conditions. It is important that the sample be properly taken in a quality-controlled manner for submission to a laboratory and that the sample be representative of the area being sampled [s].

b) **Samples must be collected and stored such that degradation or alteration of the sample is minimized**. Collect the sample in a clean, polyethylene or glass container, taking care to fill it completely to exclude any air and tightly cap immediately after sampling. **The samples must be unpreserved and cooled at 4°C**. The sample should be examined as soon as possible, preferably within 2 hours, as any delay could cause a pH change due to ongoing chemical reactions in the water system. It is recommended the holding time not exceed 24 hours, **and it is mandatory that the holding time not exceed 72 hours from the time of sampling. Results reported beyond holding times must be flagged as not reliable.**

c) Samples must be clearly labeled with the date and time of sampling, location or source of the sample, type of sample (grab or composite), analysis required and the identity of the individual who collected the sample. Labels must be filled out in indelible ink and fixed to the sample container such that they will not fall off when wet or during transport.

Apparatus

a) pH/ion meter capable of reading to 0.01 pH units, with a printer (not necessary but highly recommended). Table 1 provides the most important characteristics of four typical pH meters commercially available (note that [a] defines the various pH meter types listed in Table 1). Choice of electrodes will depend on the desired precision of measurement [a].

Table 1 Laboratory pH Meter

	Type I	Type II	Type III	Type IV
Range - Normal - Expanded	0 to 14	0 to 14 2 pH units	0 to 14 1.4 pH units	0 to 14.000
Scale Division	0.1	0.01	0.01	0.001
Accuracy	±0.05	±0.01	±0.007	±0.002
Repeatability	±0.02	±0.005	±0.002	±0.002
Temperature Compensation Manual or Automatic Range °C Smallest Graduation °C	 Yes 0 to 100 2	 Yes 0 to 100 2	 Yes 0 to 100 2	 Yes 0 to 100 2
Slope Compensator	-	Yes	Yes	Yes

b) *Reference Electrode*: consisting of a half cell that provides a constant electrode potential. Commonly used are calomel and silver: silver-chloride electrodes. Either is available with several types of liquid junctions. Asbestos fibre electrode junctions are not recommended for strongly basic solutions. Follow the manufacturer's recommendation on use and care of the reference electrode [c].

c) *Glass Electrode*: The sensor electrode is a bulb of special glass containing a fixed concentration of HCl or buffered chloride solution in contact with an internal reference electrode. Several types of glass electrodes are available [c].

d) Combination electrodes incorporate the glass and reference electrodes into a single probe. It is recommended a "low sodium error" electrode be employed for measuring pH over 10 because standard glass electrodes yield erroneously low values. It is recommended that liquid membrane electrodes be employed for measuring pH below 1, since standard glass electrodes yield erroneously high values [c].

e) Temperature Sensor/probe for automatic temperature compensation (if available) with a sensitivity of at least 0.1 °C is highly recommended, **otherwise results must be temperature corrected.**

Reagents

a) Reference buffer solutions: commercially available buffers that are directly traceable to primary National Institute of Standards and Technology (NIST) standards are acceptable. The following buffers are recommended: pH 4.00, 6.00, 7.00, 8.00, 10.00 (pH values at 25 °C). Expiry dates of reference solution are labelled on the bottle; **do not use after the expiry date**.

b) For Low Ionic Strength electrodes, Orion Low Ionic Strength (LIS) Calibration Buffers and pH Ionic Strength Adjustor (ISA) are recommended.

Procedure

a) Selection of the Electrode Used:

It is imperative the analyst select the appropriate type of electrode to use for the types of samples they are measuring. Most rivers, lake waters and precipitation (rain) samples in British Columbia are low ionic strength (LIS), and require the use of LIS electrodes, LIS buffers and LIS methods.

b) Electrode Conditioning and Inspection:

Follow manufacturer's instructions for pH meter and for storage and preparation of electrodes for use. Recommended solutions for short-term storage of electrodes vary with type of electrode and manufacturer, but generally have a conductivity greater than 4,000 µS/cm. Type 1 water is a better substitute than distilled water. pH 4 buffer is best for the single glass electrode and saturated KCl is preferred for calomel and Ag/AgCl reference electrode. Saturated KCl is preferred solution for a combination electrode. pH meters and electrodes should be functionally tested before they are used in the field.

1) Conditioning of Combined Electrode:

Follow manufacturer's instructions for conditioning/reconditioning the electrode of choice.

- Check for air bubbles. Make sure that no air bubbles are trapped in the KCl crystals, and that no bubbles are present in the glass bulb and below the reference stems. If so, release bubbles by gently tapping the electrode with a finger or by swinging it in circles.

- Visually inspect to ensure glass membrane has not been damaged during storage or transport. Replace probe if necessary.

- **If conditioning of the pH electrode does not produce satisfactory results, replace the electrode**. The lifetime of the electrode is dependent on the type of samples analysed. Typical electrode lifetimes range from 6 month to 1.5 years.

c) Electrode Calibration:

Follow manufacturer's instructions for pH meter instrument calibration.

Note 1: Temperature of calibration buffers/solutions and the samples should be the same (± 0.5°C) otherwise temperature correct especially when taking field pH measurements.

1) Print out data where practical or record the results.

d) pH Measurements:

1) Follow manufacturer's instructions for pH meter measurements.

2) Measurement of High Ionic Strength (HIS) Solutions: It is recommended that a sample cup of Type 1 water ready to be used to rinse the electrode, stirrer and temperature probe assembly, between samples. **Change the rinse water frequently to minimize contamination due to carryover**. Sample carry over has resulted in major data loss.

3) Measurement of Low Ionic Strength Solutions: Perform calibration by using for example an Orion Ross Electrode (Model 81 - 02) and Low Ionic Strength Buffers. Transfer an aliquot of sample into a sample cup. Add 400 ml of Orion pHisa Ionic Strength Adjuster [f]. Perform pH measurements.

Note: 1. Do not wipe the electrode since contamination or polarisation may occur, gently dab.

2. Do not perform conductivity and pH measurement simultaneously on Low Ionic Strength samples since the diffusion of the reference electrode fill solution (KCl) into the low ionic strength sample and the addition of pHisa ionic strength adjuster, will both raise the conductivity.

4) Store the electrode following the manufacturer's instructions. For most pH electrodes, immerse the electrode in pH 4 buffer solution with the KCL filling hole sealed.

5) For instruments capable of measuring both pH and conductance simultaneously, it is recommended that conductance be measured before pH to avoid error due to salt contamination (KCl) from the reference electrode.

e) Field pH Measurements:

1) **Calibrate the instrument according to manufacturer's instructions prior to use in the field**. Ideally the temperature of the calibration solutions (buffers) should be at the same temperature to that of the sample measured for pH. This may not be possible, for example, when lake depth profiles are taken. The temperature in this case should be measured and pH values temperature corrected manually if the instrument does not have temperature compensation. If it does have temperature compensation, the results should be checked.

Avoid subjecting the field instruments to extreme environmental conditions (e.g. do not leave instrument in full sun). Allow the instrument to acclimatise to field conditions prior to field measurements.

2) Glass electrodes used for pH measurements slowly age and lose sensitivity. This can give quite erroneous results for LIS waters commonly in BC rivers and lakes. Some electrodes may only have a life time of 3-4 months. **It is important to check for loss of electrode sensitivity. This problem may not be noticed when using regular buffer solutions and therefore an extra step to check is required**. There are three ways to do this. First, to check instrument regularly from with laboratory instruments for a genuine water sample (e.g., not a buffered reference sample). Second, check it against another field instrument. Third, take a measurement of the pH prior and after the addition of KCl and the two results should be similar. If electrode is not working properly see Procedure section d) pH Measurements.

3) Electrode performance can also be determined by observing the time needed to attain a stable reading (constant pH value ±0.02 pH units for a period of 1 minute). The time required to attain stability should be less than 5 minutes for an operating electrode. If the electrode cannot attain these criterias, the electrode and/or KCl solution should be replaced.

Method Performance

a) When a two-point (or three point) calibration is performed using reference buffer solutions of pH 4.00 and pH 8.00, (or pH 4.00, 7.00 and 10.00) the electrode sensitivity (slope) should be between 98 and 102%; if it is outside the 100 $\pm$ 2 %, then re-calibrate with fresh buffers and/or check the electrode according to the manufacturer's troubleshooting guidelines/operating instructions for the electrode. **A one point calibration is not acceptable.**

b) The sensitivity of the analytical system collected over a five month period establishes (3 SD) control limits to monitor method sensitivity. Typical values obtained are listed in Appendix 1, Table 1.

c) Method Blank: Analyse an aliquot of Type 1 deionized water to monitor contamination and background interference. Typical method blank pH's are listed in Appendix 1, Table 2 but will change depending on location and supply of domestic water.

While extremely pure water would have a pH of 7.0 at standard temperature and pressure, a bottle of water left open will slowly drop to pH 5.6 as atmospheric CO_2 dissolves, forming H_2CO_3. This also serves as a check to pH electrode performance.

d) **Method Accuracy: Certified Reference Materials (CRM) or Reference Materials (RM) must be analyzed with every batch to check validity of test results, and the recovery of metals measured against the accepted or certified values.** Typical values obtained are listed in Appendix 1, Table 3.

e) **Method Precision: Duplicates must be analyzed with every batch.** Precision is determined using Relative Percent Difference (RPD). See Appendix 2 for algorithms. Typical values obtained are listed in Appendix 1 Table 4 for Single Analyst and Appendix 1 Table 5 for Multiple Analyst.

f) The calibration of the analytical system may be verified using in-house QA standard; data collected over several months establishes control limits (3 SD) to monitor method accuracy. Typical values obtained are listed in Appendix 1 Table 6.

g) **The ministry preferred Data Quality Objectives (DQO's) are listed in Appendix 2, Table 1**.

Quality Control

a) **Before analyzing any samples, the laboratory must demonstrate that the selected analytical methods can provide valid data under practical conditions in the laboratory. The laboratory should have in place a method validation process and data to demonstrate that validation has occurred and that the methods chosen can meet the data quality objectives.**

b) **Perform the appropriate two-point or three-point calibration not less than once a day**, and preferably every 3 to 4 hours.

c) **At minimum, for each batch of samples, randomly select one sample to be analysed in duplicate; also include a pH reference solution/standard and blank (that lies within the calibration range) as a check standard.**

d) Quality control procedures are essential to ensure data quality and to monitor the accuracy and precision of the instrument.

e) Detail and document any non-conformances.

f) The uncertainty of the results, detection limits, selectivity of the analysis, and its robustness in the hands of different staff should be tested and documented. Techniques used for validation include results obtained on certified or other reference materials, comparison of results with data obtained using other methods, inter-laboratory comparison data, systematic assessment of factors which could influence the results, and assessment of uncertainty based on accuracy and precision. The influence of instrumental, human and environmental factors should be considered.

g) **Assess whether the method shows statistical control by considering:**

- **the range of duplicate results, to monitor precision.**
- **the measured pH of the check standard, to monitor accuracy.**

If any parameter lies outside the established (3 SD) *control limits* OR if two consecutive parameters lie outside the (2 SD) *warning limits*, then re-calibration and/or an instrument check may be necessary. Document any non-conformance and the action taken.

Calculations and Data Processing

The pH results are reported to the nearest 0.01 pH unit.

References

a) American Society for Testing Materials, D 1293-84: "Standard Test Methods for pH of Water," in *1993 Annual Book of ASTM Standards, volume 11.01: Water (I*), pp.324-332. ASTM, Philadelphia, Pennsylvania, 1993.

b) Westcott, C.C., pH Measurements. Academic Press, New York, 1978.

c) American Public Health Association (APHA). 1999 *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Washington, DC: APHA, AWWA, WPCF.

d) GK2401C Combined Electrode - Operating Instructions, Radiometer Publication no. 983-489. Radiometer Analytical, Copenhagen, Denmark (1984).

e) ION83 Ion Meter - User's Handbook, Radiometer Publication no. 983-470. Radiometer Analytical, Copenhagen, Denmark (1984).

f) Orion Application Information: Procedure No. 501, pH Measurement in Low Ionic Strength Solutions. Orion Research Incorporated, Boston (1990).

g) General Requirements for the Competence of Testing and Calibration Laboratories, ISO 17025, the International Organization for Standardization (ISO) and the International Electrotechnical Commission (IEC), 1999.

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i) Metcalf, Richard C., Accuracy of Ross pH Combination Electrodes in Dilute Sulphuric Acid Standards. Analyst, Vol. 112 pp. 1573-1577, November 1987.

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k) Metcalf, Richard C., David V. Peck and Lori J Arent, Effect of Potassium Chloride Additions on pH Measurements of Dilute Sulphuric Acid Standards, Analyst, Vol. 115, pp. 899-904, July 1990.

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n) McQuaker, Neil. R., P.D. Kluckner and K. Sandberg, Chemical Analysis of Acid Precipitation: pH and Acidity, Limnol. Oceanogr., 24, 1979, pp. 1161-1165.

o) Stapanian, Martin A., and Richard C. Metcalf, State of the Art pH Electrode Quality Control for Measurements of Acidic, Low Ionic Strength Waters, Journal of Chemical Education, Vol. 67, No 7, 1990, pp. 623-626.

p) Presley, Richard, The Sometimes Maddening Science of pH Measurement, American Laboratory, News Edition, Vol 31, No. 13, June 1999, pp. 10-11.

q) The Inspector's Field Sampling Manual: A Sampling Manual and Reference Guide for Environment Canada Inspectors. 1st Edition ISBN 0-662-23513-4, 1995.

r) US Environmental Protection Agency, Guide to Method Flexibility and Approval of EPA Water Methods, Office of Science and Technology and Office of Water, Washington, DC, December 1996.

s) The Inspector's Field Sampling Manual: a sampling manual and reference guide for Environment Canada inspectors. 1st Edition ISBN 0-662-23513-4, 1995.

t) The Inspector's Safety Guide: a field guide for Environment Canada inspectors. 1st Edition ISBN 0-662-23533-9, 1995.

Revision History

June 2000:	Method Introduction.
November 2002:	Method incorporated into main Laboratory Manual: reformatted to match style of 2003 Lab Manual format.

pH, Electrometric, Soil and Sediment – Prescriptive Method

Parameter

pH

Analytical Method

Electrometer

Introduction

Measurement of pH is one of the most common and crucial tests in standard soil analyses. Technically, pH is the negative logarithm of the hydrogen ion activity. Many soil chemical and biological reactions are controlled by the pH of the solution in equilibrium with the soil particle surfaces.

Method Summary

This method is not Performance Based. All elements of the method must be followed as described.

A previously dried and sieved (2mm, mesh size 10) sample is diluted in 1:2 ratio with reagent grade deionized water (higher ratios may be required for high organic content samples). Sample solution is mixed by mechanical techniques (e.g. by shaking on mechanical shaker or stirring with glass rod) for 30 minutes and let stand for approximately 1 hour. The resulting supernatant is then measured using a combination electrode with a milli – volt meter.

MDL and EMS Codes

Analyte	MDL / Range	EMS Code
pH	Range 0.1 – 14	

Matrix

Soil, sediment.

Interferences and Precautions

Temperature effects and coating of the electrode with oily material are interferences. Samples with very low or very high pH may give incorrect readings. Other interferences include those listed in the British Columbia Environmental Laboratory Manual method "pH, Electrometric, Performance Based Method".

Sample Handling and Preservation

Collect soil samples in suitable containers. Polyethylene or Glass are recommended. Samples must be unpreserved. Store cool (4°C).

Stability

Holding Time: Indefinite from time of sampling until start of leachate procedure. Leachates should be analyzed within 2 hours of their preparation, and must be analyzed within 8 hours of preparation.

Procedure

Preparation of Soil Samples

Prior to leach procedure and measurement, samples are prepared as per BC MWLAP's Strong Acid Leachable Metals (SALM) in Soil method. Samples may be air dried or oven dried at ≤ 60 ± 5°C. Friable materials should be disaggregated with gentle mechanical action prior to sieving through a 10 mesh (2mm) sieve (do not use a mechanical grinder). Where available, it is recommended that a minimum of 25 grams of sieved sample be obtained for this analysis. As per the SALM method, it is permissible to omit the drying step and perform the sieving and water leach procedure on a wet sample. In this case, the amount of water present in the sample should be taken into account (an estimate is acceptable) when determining the amount of

deionized water to be used in the water leach procedure such that the recommended ratio of water to soil is met.

Water Leach Procedure

To a sample of soil in a beaker or plastic cup (20 g are recommended), add 2 mL of deionized water for each gram of dry soil and mix intermittently for a minimum of 30 minutes. Allow the soil suspension to stand until most of the suspended solids settle (recommended time is 1 hour), or use filtration or centrifugation.

Samples high in organic content may absorb most or all of the reagent water when the standard 2:1 water:soil ratio is used. If this occurs, increase the ratio of water to soil until sufficient supernatant is obtained for the pH measurement.

If the supernatant is multiphasic, decant the oily phase and measure the pH of the aqueous phase.

pH measurement

Refer to the BC Lab Manual method "pH, Electrometric, Performance Based Method" for guidance and requirements related to measurement of pH in the leachate. A summary of the requirements of this method follows:

Electrode calibration must be performed at a minimum of 2 pH values using certified reference buffer solutions (e.g. traceable to the National Institute of Standards and Technology). Buffers of pH 4 and 7 are recommended for calibration. Measure the pH of the supernatant following the pH meter manufacturer's instructions for pH measurements. Immerse the electrode into the suspension. Allow the reading to stabilize and record the value. If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected for temperature.

Quality Control

Summary of QC Requirements

QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	Not applicable	Not applicable
Reference Material (soil)	Optional	Not specified
Laboratory Duplicates	Approximately 5-10%	± 0.20 pH units

* Laboratories should report qualified data when DQOs are not met.

Method Blank: Not applicable to this test.

Reference Materials: The use of soil RMs (e.g. in-house RMs) as control samples is recommended.

Laboratory Duplicates: Required. Replicate all components of the test from start to finish. Random duplicate selection at an approximate frequency of 5-10% is recommended.

Refer to the British Columbia Lab Manual method "pH, Electrometric, Performance Based Method" for quality control requirements related to the measurement of pH in the soil leachate produced by this method.

References

a) US EPA, Test Methods for Evaluating Solid Waste Physical / Chemical Methods (SW-846), Method 9045D, Soil and Waste pH, Rev. 4, August 2002.

b) Canadian Society of Soil Science, Soil Sampling and Methods of Analysis, 1993.

c) BC MWLAP, British Columbia Environmental Laboratory Manual for the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Ambient Air Samples, 2003.

Revision History

March 31, 2005: First version published in BC Lab Manual.

Appendix 1

Table 1: Method Sensitivity

Reference pH	N	% Sensitivity Mean	% Sensitivity Std Dev	% Sensitivity CONTROL LIMITS Lower	Upper
4.00 to 10.00	109	98.80	0.52	94.12	103.48

Table 2: Method Blank

	N	Expected pH pH Units	Measured pH pH Units	Std. Dev.	Control Limits
Blank	316	N/A	6.16	0.17	± 0.50

Most data from the blanks run at Env. Canada (PESC) prior to May 1999.

Table 3: Method Bias

Certified value / pH units	N	Measured pH mean	Std. Dev.	% Bias	Significant (95% CL)
{**a**} 9.08 ± 0.20	3	9.031	0.011	- 0.54	No
{**b**} 6.97 ± 0.03	6	6.922	0.005	- 0.69	No
{**c**} 9.05 ± 0.20	5	9.022	0.021	- 0.31	No

Most data from the certified reference solutions run at Env. Canada (PESC) prior to May 1999.

{**a**} pH standard by Environmental Resource Associates. Lot #9967.
{**b**} Low Ionic Strength pH buffers by Orion Research. Lot #YX1.
{**c**} pH standard by Environmental Resource Associates. Lot #9964.
CL - Confidence Limit.

Table 4: Single Analyst Method Precision

Sample Type	N	pH Mean	Std Dev	% RSD
Mine Effluent	5	7.53	0.012	0.16
Sewage Effluent	5	3.57	0.140	3.91
River Water	5	7.90	0.051	0.64
Ground Water	5	8.16	0.009	0.11

Most data from the samples run at Env. Canada (PESC) prior to May 1999.

Table 5: Single Analyst (Within-Run) Precision

pH Analytical Range / pH units	No. of Sets of Duplicates	%Mean Normalized Range	Std. Dev.	CONTROL LIMITS for Normalized Duplicate Range
0 - 14	302	0.320	0.456	1.37

Most data from the duplicates run at Env. Canada (PESC) prior to May 1999.

Table 6: Control Sample Bias (Data Current to May 1999)

Reference pH	N	% Recovery Mean	% Recovery Std Dev	% Recovery CONTROL LIMITS Lower	Upper
4.00 to 10.00	315	100.06	0.278	99.11	101.43
8.78	35	99.92	0.67	97.91	101.93

Appendix 2

Table 1: Ministry Preferred DQO's

Sample Type	Range	Bias (pH Units)	Precision (pH Units)
Effluent	0-14	0.1	± 0.1
Freshwater	0-14	0.05	± 0.05
Marine	0-14	0.05	± 0.05
Precipitation (rain)	0-14	0.01	± 0.01

Phosphorus, Orthophosphate - Dissolved

Parameter

Orthophosphate, dissolved as P

Analytical Method

Automated ascorbic acid reduced colorimetric

EMS Code

a) Automated method **1118 X157**
b) Manual method (EMS code to be defined upon request)

Introduction

Phosphorus generally occurs in water as phosphates. The various classifications, orthophosphate, polyphosphates and organically bound phosphates, may occur in solution, in particulate detritus and in the bodies of aquatic organisms. Fertilizers and commercial cleaning preparations are major sources of phosphorus. This procedure measures the concentration of dissolved, reactive phosphorus present in the sample.

Method Summary

The sample is reacted with a mixture of ammonium molybdate and potassium antimonyl tartrate in acid solution. Ascorbic acid is then added to produce a blue coloured product with an absorbance maximum at 880 nm. The absorbance of the solution is measured and the phosphorus concentration is determined by comparison with standards treated in the same manner.

MDL

Typical: 0.003 mg P/L
Range: 0.003 - 1.0 mg P/L range

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

High iron concentrations cause precipitation of phosphorus. Sample turbidity must be removed by filtration prior to analysis for orthophosphate. Salt error for samples with 5 to 20% salt is less than 1%, but baseline correction is required for marine samples that are compared with fresh water standards. Arsenic concentrations > phosphorus concentration, may interfere. Glassware used in the storage and manipulation of samples for phosphate analysis should be washed in non-phosphate detergents and rinsed with hot dilute HCl and then several times with distilled/deionized water.

Sample Handling and Preservation

Acid washed plastic or glass bottle (50 mL required for analysis). No preservation, store cool, 4°C.

Stability

M. H. T.: 2 days.

Principle

Orthophosphate reacts with ammonium molybdate and potassium antimonyl tartrate to produce a heteropoly acid - phosphomolybdic acid - that is converted to an intensely coloured blue complex by reduction with ascorbic acid. Absorbance at 880 nm is proportional to phosphorus concentration.

Procedure

Both manual and automated versions of the procedure exist. Either a spectrophotometer for use at 880 nm with a light path of 2.5 cm or longer, or an automated analytical system incorporating a colorimeter with an 880 nm filter and 5 cm tubular flow cell is required.

Precision ±0.066 mg P/L at 0.30 mg orthophosphate P/L.

Accuracy As bias, -0.04 mg orthophosphate P/L at 0.30 mg P/L.

Quality Control Each batch should contain a 10% level each of blank and duplicate samples with a minimum of one each per batch.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 365.1 (automated) and Methods 365.2 & 365.3 (manual).
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-P F (automated) and 4500-P E (manual).

Revision History

February 14, 1994: Publication in 1994 Laboratory Manual.
December 31, 2000: SEAM codes replaced by EMS codes.

Phosphorus, Total Phosphate

Parameter

Total phosphate as P

Analytical Method

Digestion, auto, ascorbic acid reduced colorimetric

EMS Code

a) **Automated method P- - T X185**
b) Manual method (EMS code to be defined upon request)

Introduction

Phosphorus generally occurs in water as phosphates. The various classifications, orthophosphate, polyphosphates and organically bound phosphates, may occur in solution, in particulate detritus and in the bodies of aquatic organisms. Fertilizers and commercial cleaning preparations are major sources of phosphorus. This procedure measures the total concentration of phosphate species present in the sample.

Method Summary

The unfiltered sample is acidified, potassium persulfate is added and the mixture is digested at elevated temperature and pressure in a steam autoclave. After digestion, the sample is reacted with a mixture of ammonium molybdate and potassium antimonyl tartrate in acid solution. Ascorbic acid is then added to produce a blue coloured product with an absorbance maximum at 880 nm. The absorbance of the solution is measured and the phosphorus concentration is determined by comparison with standards treated in the same manner.

MDL

Typical: 0.003 mg P/L
Range: 0.003 - 1.0 mg P/L range

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

High iron concentrations cause precipitation and loss of phosphorus. Salt error for samples with 5 to 20% salt is less than 1%, but baseline correction is required for marine samples that are compared with fresh water standards. Arsenic concentrations > phosphorus concentration may interfere. Glassware used in the storage and manipulation of samples for phosphate analysis should be washed in non-phosphate detergents and rinsed with hot dilute HCl and then several times with distilled/deionized water.

Sample Handling and Preservation

Glass (50 mL) - acid washed.
No preservation, store cool, 4°C.

Stability

M. H. T.: 2 days.

Principle

Acid-persulfate digestion converts condensed phosphates and organically bound phosphorus to reactive orthophosphate. Orthophosphate combines with ammonium molybdate and potassium antimonyl tartrate to produce a heteropoly acid - phosphomolybdic acid - that is converted to an intensely coloured blue complex by reduction with ascorbic acid. Absorbance at 880 nm is proportional to phosphorus concentration.

Procedure

Both manual and automated versions of the colour development (post digestion) procedure exist. Either a spectrophotometer for use at 880 nm with a light path of 2.5 cm or longer, or an automated analytical system incorporating an 880 nm filter and 5 cm tubular flow cell is required.

Precision

±0.066 mg P/L at 0.30 mg P/L.

Accuracy

As bias, -0.04 mg P/L at 0.30 mg P/L.

Quality Control

Each analytical batch should contain a 10% level each of blank, recovery (spiked blank or reference sample) and duplicate samples with a minimum of one each per batch.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 365.1 (also 365.4 for the digestion procedure).

b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-P F (automated) and 4500-P E (manual).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Phosphorus, Total Dissolved Phosphate

Parameter

Total dissolved phosphate as P

Analytical Method

Digestion, auto, ascorbic acid reduced colorimetric

EMS Code

a) Automated method for filtered samples **P--D X158**
b) Automated method for unfiltered clear solutions **P--D X185**
c) Manual method (EMS code to be defined upon request)

Introduction

Phosphorus generally occurs in water as phosphates. The various classifications, orthophosphate, polyphosphates and organically bound phosphates, may occur in solution, in particulate detritus and in the bodies of aquatic organisms. Fertilizers and commercial cleaning preparations are major sources of phosphorus. This procedure measures the total concentration of dissolved phosphate species present in the sample.

Method Summary

The filtered sample is acidified, potassium persulfate is added and the mixture is digested at elevated temperature and pressure in a steam autoclave. After digestion, the sample is reacted with a mixture of ammonium molybdate and potassium antimonyl tartrate in acid solution. Ascorbic acid is then added to produce a blue coloured product with an absorbance maximum at 880 nm. The absorbance of the solution is measured and the phosphorus concentration is determined by comparison with standards treated in the same manner.

MDL

Typical: 0.003 mg P/L
Range: 0.003 - 1.0 mg P/L range

Matrix

Drinking, surface and saline waters, wastewater.

Interferences and Precautions

High iron concentrations cause precipitation of and loss of phosphorus. Salt error for samples with 5 to 20% salt is less than 1%, but baseline correction is required for marine samples that are compared with fresh water standards. Arsenic concentrations > phosphorus concentration may interfere. Glassware used in the storage and manipulation of samples for phosphate analysis should be washed in non-phosphate detergents and rinsed with hot dilute HCl and then several times with distilled/ deionized water.

Sample Handling and Preservation

Glass (50 mL) - acid washed. No preservation, store cool, 4°C.

Stability

M. H. T.: 2 days.

Principle

Acid-persulfate digestion converts condensed phosphates and organically bound phosphorus to reactive orthophosphate. Orthophosphate reacts with ammonium molybdate and potassium antimonyl tartrate to produce a heteropoly acid - phosphomolybdic acid - that is converted to an intensely coloured blue complex by reduction with ascorbic acid. Absorbance at 880 nm is proportional to phosphorus concentration.

Procedure

Both manual and automated versions of the colour development (post digestion) procedure exist. Either a spectrophotometer for use at 880 nm with a light path of 2.5 cm or longer, or an automated analytical system incorporating an 880 nm filter and 5cm tubular flow cell is required.

Precision

±0.066 mg P/L at 0.30 mg P/L.

Accuracy

As bias, -0.04 mg P/L at 0.30 mg P/L.

Quality Control

Each analytical batch should contain a 10% level each of blank, recovery (spiked blank or reference sample) and duplicate samples with a minimum of one each per batch.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 365.1 (also 365.4 for the digestion procedure).

b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-P F (automated) and 4500-P E (manual).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Radium, Total or Dissolved

Parameter
Radium, total
Radium, dissolved

Analytical Method
$BaSO_4$ co-precipitation, gross alpha scintillation

EMS Code

a)	Not filtered	**RA-T X331**
b)	Filtered	**RA-D X331**

Introduction
This method is applicable to the determination of alpha-emitting isotopes of radium.

Method Summary
Lead and barium carriers are added to the sample containing alkaline citrate, then sulfuric acid (H_2SO_4) is added and radium is co-precipitated with lead and barium as sulfates. The precipitate is filtered, rinsed with nitric acid (HNO_3), redissolved in alkaline EDTA, and then reprecipitated as radium-barium sulfate by adjustment of pH to 4.5. The precipitate is filtered and the radioactivity measured, after allowing time for generation of daughter products, with an alpha scintillation counter.

MDL
Typical: 0.01 Bq/L (with 500 mL sample)

Matrix
Fresh water, wastewater.

Interferences and Precautions
Other alpha-emitters, such as Bi, Po and Th, will also be co-precipitated. The trans-uranium elements will not be co-precipitated if reducing conditions are avoided.

Sample Handling and Preservation
Plastic or glass (500 mL).
Concentrated HNO_3, 4 mL/L.

Stability
M. H. T.: 28 days.

Principle or Procedure
Due to the difference in half-lives of the nuclides in the series that includes the alpha-emitting Ra isotopes, these isotopes can be determined by the rate of ingrowth and decay of their daughter products in a coprecipitate with barium sulfate.

Precision
± 28% at the 95% confidence level.

Accuracy
Recoveries ranged from 94.9% to 99.4%.

Quality Control
See reference.

References
a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 7500-Ra B.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Residue, Filterable (TDS), 1.0 µm

Parameter Residue, filterable 1.0 µm

Analytical Method Gravimetric, 1.0 µm filter

EMS Code **0007 X017**

Introduction Filterable residue (FR), also referred to as total dissolved solids (TDS), represents the portion of the that will pass through a filter of a particular size. The final result provides a measure of the dissolved mineralization in the water.

Method Summary A well-mixed sample is filtered through a standard glass fibre filter. A measured portion of the filtrate is evaporated in a preweighed evaporating vessel and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. (The filtrate from residue, non-filterable may be used.)

MDL Typical: 4 mg/L
Range: 4 mg/L to 20,000 mg/L

Matrix Drinking, surface and saline waters, wastewater.

Interferences and Precautions Highly mineralized waters with considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and will require prolonged drying, desiccation and rapid weighing. Samples with high concentrations of bicarbonates require prolonged drying. Too much residue in the evaporating dish will cause the residue to crust over and entrap water that may not be driven off during drying. Limit total residue to 200 mg.

Sample Handling and Preservation Plastic or glass (100 mL).
Cool, 4°C.

Stability M. H. T.: 14 days.

Principle or Procedure Glass fibre filter discs, 1.0 µm (Whatman 934-AH, or equivalent).

Precision ± 10% up to 250 mg/L.

Accuracy None listed.

Quality Control Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 2540 C.
b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983, Method 160.1

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Residue, Nonfilterable (TSS)

Parameter	Residue, nonfilterable
Analytical Method	Gravimetric, whole bottle, 105°C
EMS Code	**0008 X332**
Introduction	Nonfilterable residue, also referred to as total suspended solids (TSS), is the term applied to the material retained by a filter of standard pore size.
Method Summary	The entire sample is filtered, with rinsing, through a pre-weighed glass fibre filter, and the residue on the filter is dried to constant weight at 103°-105°C. The increase in weight of the filter is reported as nonfilterable residue. The filtrate may be used for residue, filterable.
MDL	Typical: 4 mg/L Range: 4 to 20,000 mg/L
Matrix	Drinking, surface and saline waters, wastewater.
Interferences and Precautions	Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. Samples high in dissolved solids, saline waters, brine, and some wastes may be subject to a positive interference. Select filtering apparatus with care, so that washing of filter and dissolved solids in the filter minimizes this potential for interference.
Sample Handling and Preservation	Whole bottle analyses - volume dependent on concentration. Store cool, 4°C.
Stability	M. H. T.: 14 days.
Principle or Procedure	Glass fibre filter discs (Whatman 934-AH, or equivalent). Drying oven at 103°-105°C.
Precision	± 10% up to 250 mg/L.
Accuracy	None listed.
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 2540 D. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 160.2.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Residue, Settleable (Settleable Solids)

Parameter	Residue, settleable
Analytical Method	Imhoff cone, volumetric
EMS Code	**0023 1010**
Introduction	Settleable residue, also referred to as settleable solids, is the term applied to particulate material that will settle out of suspension over an arbitrary time period.
Method Summary	A well mixed sample is introduced into a graduated Imhoff cone and allowed to stand for an hour (with gentle spinning of the cone at 45 minutes to minimize entrapped pockets of water). The volume of settled residue is recorded and reported as mL/L.
MDL	0.2 mL/L Range: 0.2 to 40 mL/L (limit of Imhoff cone graduation)
Matrix	Surface and saline waters; domestic and industrial wastes.
Interferences and Precautions	Floating material, such as leaves and sticks, is not to be included. Pockets of liquid may occur between large settled particles; the volume of these should be estimated and subtracted from the total.
Sample Handling and Preservation	Bottle: 0.5 to 4.5L glass or plastic. Preservation: none. Store cool, 4°C.
Stability	M. H. T.: 14 days.
Principle or Procedure	Imhoff cone graduated from 0.2 to 40 mL and at 1 L.
Precision	None listed.
Accuracy	None listed.
Quality Control	The procedure is not amenable to standard QA/QC techniques such as blanks, replicates and spikes.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 2540 F. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 160.5.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Residue, Total (TS)

Parameter	Residue, total
Analytical Method	Gravimetric, 180°C
EMS Code	**0005 X333**
Introduction	Total residue, also referred to as total solids, is the term applied to the material residue left in the test vessel after evaporation of free water. It includes both suspended and dissolved matter.
Method Summary	A well mixed sample is evaporated in a pre-weighed dish and dried to constant weight in the oven at 180°C. The increase in weight over the empty dish represents the total solids. Total solids is the sum of homogenous suspended and dissolved materials in a sample.
MDL	Typical: 10 mg/L Range 10 mg/L to 20,000 mg/L
Matrix	Drinking, surface and saline waters, wastewater.
Interferences and Precautions	Non-representative particulates such as leaves, sticks, fish and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result. Floating oil and grease, if present, should be included in the sample and dispersed by a blender device before sub-sampling.
Sample Handling and Preservation	Plastic or glass (100 mL). Store cool, 4°C.
Stability	M. H. T.: 14 days.
Principle or Procedure	Drying oven at 180°C. Porcelain or Pyrex evaporating dish (100 mL).
Precision	± 6.0 mg/L at various concentrations.
Accuracy	None listed.
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition 1992, Method 2540 C. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 160.3.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Residue, Total, Fixed and Volatile

Parameter
Residue, total fixed
Residue, total volatile

Analytical Method
Gravimetric, ignition at 550°C (fixed)
Gravimetric, ignition at 550°C (volatile)

EMS Code

a)	fixed, units = mg/L	**0006 1940**
b)	fixed, units = µg/g	**0006 X479**
c)	volatile, units = mg/L	**0032 1940**
d)	volatile, units = µg/g	**0032 X479**

Introduction
The loss of weight, on ignition at 550°C of residue from any of the various residue procedures, offers an approximation of the amount of organic matter present in that portion of the sample. The weight remaining is the fixed total, filterable or nonfilterable residue while the weight lost is the volatile counterpart. Volatile total residue is also referred to as volatile total solids.

Method Summary
Residue from determination of residue, total, is ignited to constant weight at 550°C in a muffle furnace. Usually, a 15 to 20 minute ignition is required. The ignited residue is cooled in a desiccator and weighed. The cycle of igniting, cooling, desiccating and weighing is repeated until a constant weight is attained. The difference between the total residue and the fixed residue is the volatile residue.

MDL
Typical: 0.1 mg/L
Typical: 4 mg/L

Matrix
Sewage, sludge, waste, and sediments.

Interferences and Precautions
A major source of error is failure to obtain a representative sample. The test subject to errors due to loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts.

Sample Handling and Preservation
0.5 to 4.5 L plastic or glass bottle, unfiltered and unpreserved. Store cool (4°C).

Stability
M. H. T.: 14 days.

Principle or Procedure
Organic matter is volatilized or combusted at 550°C.

Precision
SD = ± 11 mg/L at 170 mg/L volatile residue concentration.
Accuracy
None listed.

Quality Control
Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 160.4
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 2540 E.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Residue; Fixed and Volatile Filterable (VFR)

Parameter	Residue, volatile filterable Residue, fixed filterable
Analytical Method	Loss on ignition at 550°C Ash, 550°C
EMS Code	a) filterable, volatile, units = mg/L **RF-F F012** b) filterbale, fixed, units = µg/g **VFR- F012**
Introduction	The loss of weight, on ignition at 550°C of residue from any of the various residue procedures, offers an approximation of the amount of organic matter present in that portion of the sample. .The weight remaining is the fixed total, filterable or nonfilterable residue while the weight lost is the volatile counterpart. Volatile filterable residue is also referred to as volatile dissolved solids.
Method Summary	Residue from determination of residue, filterable, is ignited to constant weight at 550°C in a muffle furnace. Usually, a 15 to 20 minute ignition is required. The ignited residue is cooled in a desiccator and weighed. The cycle of igniting, cooling, desiccating and weighing is repeated until a constant weight is attained.
MDL	None listed. Range: None listed.
Matrix	Sewage, sludge, waste, and sediments.
Interferences and Precautions	The test is subject to errors due to loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts.
Sample Handling and Preservation	Plastic bottle (100 mL). No preservation. Store cool (4°C).
Stability	M. H. T.: 14 days.
Principle or Procedure	Organic matter is volatilized or combusted at 550°C.
Precision	SD = ± 11 mg/L at 170 mg/L volatile residue concentration.
Accuracy	None listed.
Quality Control	Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 160.4.
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 2540 E.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Residue; Fixed Nonfilterable (FNFR) and Volatile Nonfilterable (VNFR)

Parameter
Residue, fixed nonfilterable
Residue, volatile nonfilterable

Analytical Method
Gravimetric, 9cm Buchner, 550°C

EMS Code
a) FNFR **0009 1050**
b) VNFR **0010 1050**

Introduction
The loss of weight, on ignition at 550°C of residue from any of the various residue procedures, offers an approximation of the amount of organic matter present in that portion of the sample. The weight remaining is the fixed total, filterable or nonfilterable residue while the weight lost is the volatile counterpart. Volatile nonfilterable residue is also referred to as volatile suspended solids.

Method Summary
Residue from determination of residue, non-filterable, is ignited to constant weight at 550°C in a muffle furnace. Usually, a 15 to 20 minute ignition is required. The ignited residue is cooled in a desiccator and weighed. The cycle of igniting, cooling, desiccating and weighing is repeated until a constant weight is attained.

MDL
Typical: 1 mg/L

Matrix
Sewage, sludge, waste, and sediments.

Interferences and Precautions
A major source of error is failure to obtain a representative sample. The test is subject to errors due to loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics and decomposition of mineral salts.

Sample Handling and Preservation
0.5 to 4.5L plastic or glass bottle, unfiltered and unpreserved. Store **and** cool (4°C).

Stability
M. H. T.: 14 days.

Principle or Procedure
Organic matter is volatilized or combusted at 550°C.

Precision
SD = ± 11 mg/L at 170 mg/L volatile residue concentration.

Accuracy
None listed.

Quality Control
Analytical balances used for this procedure should be serviced and calibrated on a regular schedule. An instrument log should be kept.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, EMSL, Revised March 1983. Method 160.4.
b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 2540 E.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Title edited.

Salinity

Parameter	Salinity by electrical conductivity
Analytical Method	Salinometer
EMS Code	**0130 1130**
Introduction	Salinity is a measure of the mass of dissolved salts in a given quantity of solution. Due to difficulties associated with the gravimetric determination of solids, especially at higher concentrations, an indirect method is normally preferred. Electrical conductivity provides a convenient and precise approach.
Method Summary	The electrical conductance is measured using a conductivity bridge which has been calibrated with KCl solutions of known concentration. Salinity is determined by reference to the Practical Salinity Scale, 1978.
MDL	Not given. Range: 4 - 40 g/kg
Matrix	Saline water and wastewater.
Interferences and Precautions	The method assumes that samples have the same relative chemical composition as seawater. Highly mineralized groundwater and samples with high or low pH may give misleading results.
Sample Handling and Preservation	0.5 to 4.5 litre plastic bottle, unfiltered and unpreserved. Store cool (4°C).
Stability	M. H. T.: 28 days.
Principle or Procedure	A seawater with a conductivity at 15°C equal to that of a KCl solution containing 32.4356 g in 1.00 kg of solution is defined as having a practical salinity of 35.
Precision	None listed.
Accuracy	None listed.
Quality Control	None listed.
References	a) Standard Methods for the Examination of Water and Wastewater, 18th Ed., APHA, AWWA, WEF, 1992. Method 2520B.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Saturated Paste Extraction for Soils

Parameter

Water soluble salts (where saturated paste extraction is specified)

Analytical Method

Saturated Paste Soil Extraction

Introduction

This method was prepared for the British Columbia Ministry of Water, Land and Air Protection (BCMWLAP), specifically to assess the concentrations of sodium and chloride in soil samples. However, it can also be used to assess other ionic components of concern in soil.

Soluble salts are removed from the soil sample using a saturated paste aqueous extraction. Ionic components in the extract are determined using analytical techniques appropriate for water samples.

This method is applicable to soils, which are defined by Carter as the "minus 10 mesh" fraction (<2mm). It is not applicable to gravels or other samples where the particle size is predominantly >2mm.

Method Summary

This method involves adding a known quantity of deionized water to a soil sample until saturation is achieved. The sample is allowed to stand for at least 4 hours and the aqueous extract is recovered for analysis.

This method is performance-based. Alternate fixed extraction ratios may be employed for a given soil type at a given site if specified requirements are met.

MDL

Method Detection Limits (MDLs) are dependent on soil texture (saturation percentage), and on the techniques used for ionic determinations.

Matrix

Soil, sediment, solids.

Interferences

The interferences encountered will differ depending on the analytical technique used to analyze ionic components in the extract. Analysts should be aware of the limitations of each methodology.

Sample Handling

Use a clean polyethylene or glass container for sample collection. Plastic bags are also suitable. Store samples at room temperature. Conduct extraction within 6 months of sample collection, or within the holding times for any required determinative tests.

Apparatus

Beakers with covers, glass or polyethylene;
Vacuum filtration apparatus;
Filters, cellulose or glass fiber are suitable;
Drying oven;
Electronic balance.

Reagents

Reagent water, distilled, deionized or equivalent.

Applicability

The Standard Procedure described below is applicable to most soil samples, except for the following categories:

- Samples that are predominantly gravels.
- Samples that are over-saturated with water.
- Samples that are oily wastes.

Refer to modified procedures below for definitions and processing instructions for gravels and over-saturated samples. This method is not applicable to oily wastes, where the oil content is such that a saturated paste cannot be formed.

Standard Procedure

1) Homogenize the complete soil sample, including any overlying water, then take a sub-sample of approximately 200 to 400 g of the wet soil. Lesser amounts may be used if sufficient filtrate can be recovered for the required analyses. Air or oven dry the soil at less than (60+/-5)°C.

   Note: The 60°C maximum drying temperature is adopted from, and consistent with, the BC WLAP method for Strong Acid Leachable Metals.

2) Use a mechanical grinder to grind the soil to pass through a 2mm screen. The soil should not be subjected to sufficient force or abrasion to break up rocks, or the individual sand, silt, or clay particles. Discard the >2mm fraction.

   Note: The drying and/or grinding steps may be omitted for samples that can readily be made to form a saturated paste without these steps. These steps are particularly important for samples with high clay content. The sieving step may be omitted for samples that clearly have a minimal fraction >2mm.

3) Weigh the soil into a container with a cover. Record the total weight of the container and soil sample.

4) If the soil was not dried before weighing, determine soil moisture content on a separate soil aliquot.

5) Add sufficient deionized water while mixing to saturate the soil sample. At saturation, the soil paste glistens, flows slightly when the container is tipped, and slides cleanly from a spatula. A trench carved in the soil surface will readily close upon jarring the container.

6) Allow the covered sample to stand for at least 4 hours and check to ensure the saturation criteria are still met. If free water has accumulated on the surface, add a weighed amount of soil and remix. If the soil has stiffened or does not glisten, add deionized water and mix thoroughly. After any additional water or soil is added, allow the sample to equilibrate for at least one hour to ensure that a satisfactory end-point has been attained. Peat soils may require an overnight wetting period to obtain a definite endpoint for the saturated paste.

7) Weigh the container and its contents. Record the increase in weight, which corresponds to the amount of water added.

8) Collect the extract using vacuum filtration until air passes through the filter. Use a highly retentive filter paper (e.g. Whatman #5). Turbid filtrates should be refiltered or centrifuged and decanted. Alternatively, a filter press may be used.

9) Store extracts at 4°C. For metals analyses only, preserve a portion of the extract with nitric acid to < pH2. Analyze before the holding times which pertain to each determinative test.

10) Methods for determining ion concentrations in the liquid extract should be based on those listed in the BCMWLAP *British Columbia Environmental Laboratory Manual* or equivalent validated methods.

Procedure for Gravels

For the purposes of this method, gravels are defined as any sample with greater than a 50% component by weight of the >10 mesh fraction after disaggregation and sieving.

For gravel samples that meet this definition, use a fixed-ratio leach employing a 2:1 ratio of deionized water (mL) : dry soil sample (g).

Allow the covered sample to stand for at least 4 hours. Then proceed to steps 8 through 10 of the Standard Procedure. Centrifugation may alternatively be used for clarification of the leachate.

Reported ionic concentrations generated from this procedure should be clearly indicated as being derived from a gravel utilizing a 2:1 water leach.

Procedure for Oversaturated Soils

Analysis of water soluble salts in soil samples which are received in an over-saturated condition (i.e. over-saturated with water) are done using the filtrate as received. Proceed with steps 8 through 10 of the Standard Procedure to extract and process the leachate. Centrifugation may alternatively be used for clarificaton of the leachate.

Reported ionic concentrations generated from this procedure should be clearly indicated as being derived from the overlying water from an over-saturated soil.

Saturated paste ionic components are reported as mg/kg based on a dry sample weight.

$$\text{Saturated Paste Ion Concentration (mg/kg dry weight)} = \frac{C \times (V_1 + V_2)}{W}$$

Where,

C = concentration of ionic component in saturated extract (mg/L)
V_1 = volume of deionized water added to soil aliquot (L)
V_2 = volume of soil moisture in soil aliquot, if any (L)
W = dry weight of soil aliquot (kg)

Use of Alternative Methods

Any analytical method options selected for this analysis must meet or exceed the requirements specified in the *BCMWLAP British Columbia Environmental Laboratory Manual, Section A - Laboratory Quality Assurance / Quality Control Guidelines*. Control limits for precision and accuracy of measurement are at the discretion of the laboratory.

There is provision within the framework of the BC CSR to allow for performance based measures in key areas. In the case of extraction of salts from soils, alternate procedures to the saturated paste extraction procedure may be employed.

It is recognized that some investigators employ fixed ratio extractions of water to soil. These can be more convenient to use, can yield higher extraction volumes, and in many cases reliable correlations may exist with the saturated paste extraction procedure for certain soil types.

It is required that alternate methods be confidently related to the saturated paste ion concentration on a site-specific and soil-type specific basis. This requires that representative numbers and types of soil samples have been analyzed using the saturated paste technique and any alternate technique, and that a clearly defined mathematical relationship exists.

Those wishing to use alternate techniques to a saturated paste extract technique must demonstrate this relationship for each major soil type encountered at a given site. As a minimum requirement, at least eight soil samples from each soil type at a given site must be analyzed as a basis for regression analysis. Acceptable alternative methods must achieve a correlation with $R^2 > 0.98$. All equivalence study results must be well-documented and retained by the laboratory and/or CSR practitioner for at least 5 years in the event of audit.

Once an acceptable correlation has been determined, the appropriate correction algorithm must be applied to all subsequent data for the site to convert ionic concentrations to their saturated paste equivalent values.

Laboratories must disclose to their clients, and CSR practitioners must disclose to the ministry where alternative extraction techniques to saturated paste have been employed.

Quality Control

Method Blanks: Analyze at least one with each sample batch.
Duplicates: Analyze at a frequency of approximately 10%, or one per batch.
Spikes: Not Required.

References

Carter, Martin R. (Editor), *Soil Sampling and Methods of Analysis, Section 18.2.2 Saturation Extract (Rhoades 1982*), pp. 162-163, Lewis Publishers, Boca Raton, 1993.

Bright, Doug A., and Jan Addison. *Derivation of Matrix Soil Standards for Salt Under the British Columbia Contaminated Sites Regulation*. Report to the British Columbia Ministry of Water, Land and Air Protection, Ministry of Transportation and Highways, British Columbia Buildings Corporation and Canadian Association of Petroleum Producers, 2002.

Gartley, Karen L., Recommended Soluble Salts Tests. Recommended Soil Testing Procedures for the Northeastern United States, 2nd edition, Northeastern Regional Publication No. 493, Agricultural Experiment Stations of Connecticut, Delaware, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island, Vermont, and West Virginia, December 15, 1995.

Alberta Energy and Utilities Board. Guide 50: Drilling Waste Management, section 3, pp 3-5, October, 1996.

BC Ministry of Water, Land and Air Protection. *Strong Acid Leachable Metals in Soil – Performance Based Method.* British Columbia Environmental Laboratory Manual for the Analysis of Water, Wastewater, Sediment, Biological Materials and Discrete Air Samples, 2003 edition.

Revision History

First Revision March 31, 2005

Determination of Site-Specific Soil-Water Partitioning Co-efficient (Kd) for Chloride (Prescriptive Method)

Parameter

Soil Adsorption Co-efficient (Kd) for Chloride.

Analytical Method

Calculation of Kd value for chloride requires the indirect measurement of chloride ion concentration that is retained on soil particles of a particular soil sample, as well as a direct measurement of the concentration of chloride ions in the interstitial water of the soil at equilibrium.

Chloride analysis is by any approved analytical method with sufficient precision and sensitivity to meet the Performance Requirements of the method.

Introduction

The BC MOE groundwater fate model, used to predict the movement of contaminants in subsurface soils via groundwater-mediated transport, requires an estimation of how a substance partitions between soil particles and the surrounding soil interstitial water (Soil Adsorption Coefficient: Kd). This in turn influences the degree to which a substance is retarded in its transport in the saturated zone, relative to the expected groundwater velocity.

BC CSR Soil Matrix Standards (Schedule 5) for either drinking water or aquatic life protection are back-calculated soil concentrations estimated in part using a range of plausible Kd values. This method is intended to provide an estimate of actual site-specific Kd - Chloride values, which in some cases may provide some release from the Standards.

Kd is defined as the ratio of the contaminant concentration associated with the solid (µg substance/ g dry soil) to the contaminant concentration in the surrounding aqueous solution (µg substance / mL solution) when the system is at equilibrium. The units for Kd therefore are mL/g or similar.

$Kd\ (mL/g) = A_i / C_i$

Where:
A_i = adsorbate concentration on the solid at equilibrium (µg/g).
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (µg/mL).

The (draft) BC Matrix Numerical Soil Standards for Chloride utilize the following five categories for Kd Chloride: 0-0.05 mL/g, 0.05-0.10 mL/g, 0.10-0.15 mL/g, 0.15-0.20 mL/g, and ≥0.20 mL/g.

Chloride is often considered to be a conservative tracer of groundwater movement by hydrogeologists, and is often assumed to have a Kd value of 0.0 mL/g. There is some evidence, however, that viable mechanisms for the limited adsorption of chloride to soil particles exist. On a site-specific basis, therefore, Kd values in to range of 0.05 to 0.20 may be possible.

In the absence of a reasonable scientific knowledge base, it is assumed that coarse, low organics soils (e.g. sands and coarse glaciofluvial materials) would exhibit very limited ability to retain chloride ions. Soils that include less than 10% by weight of soil fractions with a least some potential to transiently retain chloride ions (clays, organic matter, complex oxides) are likely to exhibit chloride Kd values

of zero. On the other hand, it is conceivable in the absence of better scientific information that medium-grained (10 to 30% clay/organic matter/oxide content) to fine (> 30% clay/organic matter/oxide content) to fine-grained soils would exhibit Kd values that could approach 0.10 mL/g or higher.

It has long been recognized that the Kd values for any potentially ionic substance will vary as a function of soil and groundwater pH, as well as soil properties (proportion of soil particles with negatively or positively charged chemical ligands on and extending from the exterior surface, including clays, organic matter such as humic substances, or some carbonate- and phosphate-containing minerals). Whereas the degree of soil adsorption tends to decrease at lower pHs for many cations such as cupric ion (Cu^{2+}), anions such as Cl^- or HSO_4^- tend to exhibit less soil adsorption at higher pHs (more alkaline soils).

Most soil particles are negatively charged, but some anions are also bound by, for example, metal oxides or hydroxides (MO or MOH). In particular, at relatively low pH, metal oxides can react as follows:

$MOH + H^+ \leftrightarrow MOH_2^+$
$MO + H^+ \leftrightarrow MOH^+$

Soil organic matter, including humic and fulvic substances, may also have functional groups, which form positive sites: e.g. $R\text{-}H_3^+$. These positive functional groups collectively contribute to an anion exchange capacity of soils, which can be experimentally measured. Overall, the anion exchange capacity of soils is likely to be much lower than the cation exchange capacity (i.e. – typically 5% or less of the CEC), but may nonetheless be closely related to chloride ion soil sorption tendency.

Because chloride ions have a very limited potential to adsorb to soil particles, the measurement of Kd for chloride presents challenges that are different from the vast majority of other inorganic or polar organic substances (primarily due to measurement uncertainty). This method was specifically developed within British Columbia for undertaking chloride Kd determinations.

For further information on this topic, please refer to "*Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulations*", June 2002, Doug A. Bright and Jan Addison (Report to BC WLAP, MOTH, BCBC, and CAPP), and to "*Determination of Site-Specific Soil-Water Partitioning Co-efficients (Kd) for Inorganic Ions and Polar Substances other than Chloride*" (BC Environmental Lab Manual).

Method Summary

Test samples are oven dried at low temperature, and 8 x 20g portions of the sample are equilibrated for 7 days with 20 mL volumes of deionized water or site groundwater containing sodium chloride at 320 mg/L, 1,000 mg/L, 3,200 mg/L, and 10,000 mg/L (alternative spike levels may be used where leachable native chloride for a sample exceeds 100 mg/L). Four Control Samples are prepared with the same spiking solutions, but without the test soil, to act as relative indicators of adsorption. Two Soil Blank Samples are prepared by mixing the soil with deionized water, to determine chloride background levels. Samples are centrifuged and filtered prior to analysis of the equilibrated aqueous fraction by an appropriately sensitive and precise analytical method for chloride (e.g. Ion Chromatography or Colorimetry). Adsorption co-efficient values are calculated for each of the 8 Spike Samples. Grubbs outliers are removed if necessary, and a final average Kd value is determined. A measurement uncertainty value is calculated for the Kd value to determine whether the Kd value is significantly different from zero.

In order to meet the requirements of the BC salt standards, this method must be able to accurately determine Kd values as low as 0.05 mL/g, which is extremely challenging. In order to help achieve this objective, the following key elements have been incorporated into this method:

- The ratio of dry soil weight to aqueous spike solution volume for test sample equilibrations has been maximized (defaulting to 1:1), as this ratio has a direct factor on the sensitivity of the Kd determination.
- Final Kd estimates are determined by averaging up to 8 (or more) independent Kd test measurements, performed at 3 - 4 different chloride concentrations.
- Control Spike solutions are used, such that relative adsorption values can be measured (as opposed to absolute comparisons with nominal target values).

A Measurement Uncertainty value is calculated for every Kd result determined by this method, which acts as a check on the relevance of the final result.

MDL and EMS Codes

Analyte	Approx. MDL (units)	EMS Code
Kd (Chloride)	0.05 – 0.10 mL/g *	

Achievable MDLs for this method are sample dependent, and are related to measurement uncertainty calculations that must be conducted for each Kd test result.

Matrix

Soil samples, collected as being representative of subsurface soils along groundwater flow paths. Soil Samples must not be heavily contaminated with chloride, hydrocarbons, or other contaminants.

Interferences and Precautions

Obtaining representative and valid results is dependent on performing the following procedure exactly as written. Deviations from this method will likely result in erroneous data.

The primary difficulty with this method is related to analytical precision and measurement uncertainty. Under the stated conditions of this method, a 5% error in the measured ratio of 2 analytical results (Spike Sample Results versus Control Sample Results) translates to an error in Kd value equal to at least 0.05 mL/g.

Sample Handling and Preservation

No preservation is required.

Stability

Holding and Storage Time and Particulars: Soils may be stored refrigerated at 4°C, or (preferably) frozen at approximately –20°C, for up to 28 days.

Soil anion exchange capacity is highly pH dependent. Handling and storage conditions should not alter soil pH or anion exchange capacity.

Positively charged amino acids may also occur on soil organic matter. The prescribed storage conditions should limit microbial activity. Much of chloride ion exchange sites are expected to reside on longer chain, complex, and relatively non-labile organic matter (humics, fulvics), so effects of shorter term heterotrophic microbial activity during storage should be minimal.

Procedure

1. Selection of Soils for Analysis

It is the responsibility of the submitter to provide samples that adequately capture the range of site conditions of interest, including spatial and vertical variations in soil texture or other properties which may influence groundwater flow and groundwater quality. Typically, the soil samples will have originated in connection with the assessment and/or environmental risk assessment of salt contaminated sites (e.g. from produced water releases or road salt storage/release).

Chloride Kd determinations must be conducted on soil samples representative of the site (and strata within it) but which are not contaminated with salt ions or other contaminants.

2. Drying and Preparing the Test Soil

Dry the test soil completely by spreading it thinly in a large beaker, and placing it in a 60°C drying oven for at least 16 hours (or to constant weight). A minimum of 220 dry grams will be required for each test sample.

Disaggregate the soil and sieve through a 10 mesh sieve. Do not mechanically grind the soil. Discard the > 10 mesh fraction.

3. Determination of Leachable Native Chloride in Test Soil

Weigh (20.0 $\pm$ 0.2) grams of the air-dried soil sample into a 50 mL glass or Teflon round-bottom centrifuge tube. Then add (20.0 $\pm$ 0.2) mL of deionized water to the centrifuge tube.

Check to ensure that 20 mL of water is sufficient to cover and saturate the soil. If necessary, add more water as required to permit the removal of approximately 1 - 2 mL of the aqueous solution for analysis of chloride ion concentration (after centrifuging) at the completion of the test. Record the soil weight used, and the amount of water added to the sample (to 3 significant figures). Cap tightly.

Agitate the slurry for 2 hours by mechanical shaking. Centrifuge and remove a small portion of the leachate for chloride analysis. Filter the leachate through a dry, non-contaminating 0.45 µm polycarbonate-membrane syringe filter that is known to be free of detectable chloride.

Test the leachate for chloride.

Note that this test is not applicable to samples that are contaminated with chloride (i.e. from anthropogenic chloride sources). If chloride levels in the test soil appear abnormally high, it is recommended that submitter of the test sample be contacted before proceeding. Non-contaminated samples that otherwise represent the site conditions should be obtained.

4. Optional: Testing of Site Groundwater for Chloride

The most representative Kd test results should be obtained when groundwater obtained from the site of the test sample is used as the spiking solution medium. If site groundwater is available and appropriate for use with this test, it is recommended that it be used. Otherwise, deionized water may be used. Note: Kd results using deionized water for the spiking solution are expected to be equal to or less than the Kd values that would be obtained using site groundwater.

If groundwater is to be used, approximately 300 – 500 mL will be required per test sample (more for samples with high a water holding capacity). The groundwater

must be tested for chloride prior to use (ensure the required quantity is well mixed in a single container prior to testing).

Site groundwater can only be used to prepare spike solutions that require nominal concentrations that exceed the groundwater chloride concentration. If the groundwater chloride concentration is greater than the nominal concentration required for a particular spike solution, then deionized water must be used to prepare that spike solution.

5. Preparation of Spike Solutions

If the leachable native chloride concentration from Step 3 is less than or equal to 100 mg/L, then the default spike levels specified below should be used (2 soil spikes and 1 control will be conducted at each level). If the leachable native chloride concentration from Step 3 exceeds 100 mg/L, then the spike levels should be altered such that the lowest spike level is at least 2x the leachable native chloride concentration.

Examples of Suitable Spike Concentrations as a Function of Native [Chloride]

Native [Cl]	[NaCl] Spike 1	[NaCl] Spike 2	[NaCl] Spike 3	[NaCl] Spike 4
< 100 mg/L	2 x 320 mg/L	2 x 1,000	2 x 3,200	2 x 10,000
100 – 300	2 x 1,000	3 x 3,200	3 x 10,000	-
500 mg/L	2 x 1,600	2 x 3,200	2 x 6,400	2 x 12,800

Note: For NaCl solutions, NaCl concentrations are 1.65 times Chloride concentrations as mg/L.

At least eight spikes are required, using at least 3 different spike concentrations, with no more than 3 spikes at the same level. Successive spike concentrations should increase by a constant factor of 2-4x. Examples are provided in the table above.

Prepare a sufficient volume of each spike solution for the test. For each test sample where the leachable native chloride concentration is <100 mg/L, prepare at least 100 mL each of four chloride spike solutions in deionized water at the following nominal sodium chloride concentrations: 320 mg/L, 1,000 mg/L, 3,200 mg/L, and 10,000 mg/L. These NaCl concentrations translate to chloride concentrations of 194 mg/L, 606 mg/L, 1,940 mg/L, and 6,060 mg/L. It is imperative that all spike solutions be thoroughly mixed prior to each use.

If site groundwater is used to prepare any of the solutions, the groundwater chloride concentration must be taken into account when preparing each spike solution.

Samples with high water holding capacity may require more than 100 mL of each spike solution.

6. Preparation of Spike Samples, Control Samples, and Soil Blanks.

Each Kd test requires 8 Spike Samples (using at least 3 different spike concentrations), 4 Control Samples, and 2 Soil Blanks.

Spike Samples: For each Spike Sample, weigh (20.0 $\pm$ 0.2) grams of air-dried soil sample into a 50 mL glass or Teflon round-bottom centrifuge tube.

Determine the spike solution:soil ratio that will be used for each test sample spike. Refer to the water:soil ratio that was used in Step 3 for the native chloride

leachate step. A 1:1 ratio should be used if at all possible. If a 1:1 ratio is not sufficient, determine the minimum ratio that will permit the removal of approximately 1 - 2 mL of the aqueous solution for analysis of chloride ion concentration (after centrifuging) at the completion of the test.

Add the appropriate volume of the applicable spike solution to the dry test soil in the centrifuge tube. If possible, use the default amount of (20.0 ± 0.2) mL.

Check to ensure that the spike solution fully saturates the soil after it has been completely wetted. Record the exact soil weight used, and the exact amount of spike solution added to each sample (to 3 significant figures). Cap tightly. If the actual values used are within the stated default ranges (e.g. 20.0 ± 0.2 grams or mL), then the nominal values (20 g and 20 mL) may be used for Kd calculations.

> **Note:** As the spike volume:soil ratio increases beyond 1:1, the detection limit of the Kd test will increase proportionately!

Control Samples: Add (20.0 ± 0.2) mL of each spike solution to a 50 mL centrifuge tube. Control Samples are used as a relative reference point against which adsorption of chloride by test samples is measured. Cap tightly.

> **Note:** If multiple Kd tests are being performed, the same 4 Control Samples can be used for each sample. However, each test sample and its corresponding control spike **must** be prepared from the same batch of spike solution.

Soil Blanks: For each soil sample being tested, prepare 2 Soil Blanks. Soil Blanks are used to determine the amount of chloride contributed to the test solutions from the leaching of the soil. Cap tightly.

For each blank, weigh (20.0 ± 0.2) grams of air-dried soil sample into a 50 mL centrifuge tube. Then add (20.0 ± 0.2) mL of deionized water to the centrifuge tube.

7. Equilibration of Test Samples

All test samples (Spike Samples, Control Samples, and Soil Blanks) must be mixed either with a spatula or a mechanical shaker to ensure that the soil and spike solutions are well-mixed so that contact is maximized.

Allow all test samples to equilibrate at ambient temperature for 7 days. Store samples right-side up to prevent leaking.

8. Filtration of Test Samples

When equilibration is complete, mix all samples thoroughly (e.g. using a spatula or mechanical shaker) to ensure that a representative sub-sample is taken for analysis. Centrifuge all Spike Samples and Soil Blanks to permit removal of a portion of the aqueous layer for analysis.

Remove at least 1 - 2 mL (more if accessible) of each Spike Sample, Control Sample, and Soil Blank. Filter all samples (including Control Samples) through dry, non-contaminating 0.45 µm polycarbonate-membrane type syringe filters (pre-test filters for chloride contamination potential; if necessary, pre-clean and dry filters before use).

9. Analysis of Test Samples for Chloride

Analyze all test samples for chloride using an approved, highly precise analytical procedure. If the analytical procedure employed requires more than the 1-2 mL sample volume available, or if the concentrations of the test samples exceed the range of the technique, then dilutions can be performed before analysis. Any dilutions conducted must be highly accurate (e.g. < 1% error). If a Spike Sample is diluted, its corresponding Control Sample must be diluted identically.

Any chloride test method used for this procedure must have a detection limit (after accounting for dilutions) of no more than 1 mg/L in at least the lowest concentration test samples.

During instrumental analysis, each Spike Sample (for a given spike level) must be analyzed immediately before or after its associated Control Sample. If a set of Control Samples is being applied to more than one test sample, the Control Samples must be analyzed once alongside each test sample.

The following example analysis sequence meets these requirements:

A. Calibration Standards
B. Control Standard / LCS
1. Chloride Method Blank
2. Soil Blank (Sample X)
3. Spike Sample X (320 mg/L)
4. 320 mg/L Control Sample
5. Spike Sample X (1000 mg/L)
6. 1000 mg/L Control Sample
7. Spike Sample X (3200 mg/L)
8. Spike Sample X - Duplicate (3200 mg/L)
9. 3200 mg/L Control Sample
10. Spike Sample X (10000 mg/L)
11. 10000 mg/L Control Sample
12. Calibration Verification Standard
13. Soil Blank (Sample Y)
14. Spike Sample Y (320 mg/L)
15.

10. Calculation of Kd results

For each test sample, the following measured concentrations must first be determined:

SB = Average $[Chloride]_{(aq)}$ (measured) of Soil Blank samples (mg/L)
Spk_n = $[Chloride]_{(aq)}$ (measured) of Spike Sample level n (mg/L)
CS_n = $[Chloride]_{(aq)}$ (measured) of Control Sample level n (mg/L)

Other data required to calculate Kd includes the following:

SBVol = Volume of Deionized water added to Sample Blank (mL, normally 20)
SBWt = Weight of soil used for Soil Blank sample (g, normally 20)
$SpkVol_n$ = Volume of Level n Spike Solution added to Spike level n (mL, normally 20)
$SoilWt_{SPk,n}$ = Dry Weight of Soil used for Spike level n (g, normally 20)
$CS_{nom,n}$ = nominal chloride concentration of spike solution level n (mg/L)

For each test sample, first calculate the Adsorption Fraction (AF) value for each spike level, as follows. Adsorption Fraction is the fraction of the total chloride

amount (mass) from the spike solution that was adsorbed to the soil after equilibration, expressed as a decimal fraction. AF is unitless:

$$\mathbf{AF_n = 1 - [(Spk_n - SB_{equiv}) / CS_n]}$$

where:

$$\mathbf{SB_{equiv} = SB * (SBVol / SpkVol_n) * (SoilWt_{spk,n} / SBWt)}$$

SB_{equiv} is the equivalent Soil Blank concentration that would be expected in the Spike sample due to chloride ions leaching from the sample itself. If the volumes and weights of the Soil Blank and the Spike sample are the same, then SB_{equiv} = SB. These equations assume that the amount of residual chloride adsorbed to the sample prior to spiking is small in comparison to the spike level. The adsorption fraction AF_n relates only to adsorption of chloride from the spiking solution. It is assumed that any chloride that would have leached from the unspiked soil sample (i.e. SB_{equiv}) would not re-adsorb.

Note that the nominal concentrations of the spike solutions do not enter into this calculation (therefore, error in nominal concentrations does not translate to error in the measured Kd values).

Next, the Adsorption Fraction values must be converted to Adsorption Coefficients (Kd values) as follows. This converts the amount fraction into a concentration ratio. Derivation of the formula to be used begins with the definition of Kd:

$$Kd\ (mL/g) = A_i / C_i$$

Where:
A_i = adsorbate concentration on the solid at equilibrium (mg/g)
C_i = concentration of dissolved adsorbate remaining in solution at equilibrium (mg/mL)

A_i and C_i may be calculated directly from the adsorption fraction AF_n and the nominal chloride concentration of the Control Sample and Spike Sample for each level. The A_i term represents what is sorbed to the soil mass (mg/g), calculated on the basis of mass loss from solution, divided by the soil mass in the container:

$$A_{i,n} = [AF_n\ (unitless)] * CS_{nom,n}\ (mg/L) * SpkVol_n\ (mL) * 0.001\ L/mL] / SoilWt_{Spk,n}\ (g)$$

$$C_{i,n} = [1 - AF_n\ (unitless)] * CS_{nom,n}\ (mg/L) * 0.001\ L/mL$$

Substituting the above equations for $A_{i,n}$ and $C_{i,n}$ into the Kd equation above leads to the following final equation for calculation of Kd_n. Use this equation to calculate Kd for each spike level:

$$\mathbf{Kd_n = [AF_n / (1 - AF_n)] * SpkVol_n\ (mL) / SoilWt_{Spk,n}\ (g)}$$

The units for Kd are mL/g. For each sample, Kd values are determined for each of the 3-4 spiking levels. Kd values for most samples should be near zero (typical results are expected to be in the 0.00 - 0.20 range). Although not meaningful, small negative Kd values may occur due to analytical variability.

Compute the average and standard deviation of the 8 Kd values (including any negative values obtained).

11. Outlier Checking and Calculation of Final Kd Value

If necessary, run the 8 or more Kd values for each test sample through a Grubbs outlier test using no greater than a 5% risk of false rejection. If justified, up to 2 statistical outliers may be removed by this process.

Determine the mean Kd value after removal of any outliers. Report the mean Kd result as the Kd value for the sample.

12. Determination of Measurement Uncertainty for Kd

Determine an estimated measurement uncertainty value for the mean Kd value as follows:

$$U(c) = (t_{n-1} \times s_n) / \sqrt{n}$$

Where:
U(c) = Expanded Measurement Uncertainty (minimum)
t_{n-1} = Two tailed students t value for 95% CI at n-1 degrees of freedom
s_n = The standard deviation of n final Kd results
n = The number of Kd replicates for a sample, after outlier removal

Compare the mean Kd value with the computed measurement uncertainty value. If the Kd value is less than or equal to the MU value, it should be reported as below detection limit, with the DL set equal to or greater than the calculated MU value.

13. BC MOE Reporting Requirements

All of the following results must be reported within the lab report for any test for Kd - Chloride that relates to compliance of the BC MOE Salt Standards:

- Report Kd results for all eight (or more) spikes, each reported to 3 decimal points (including any negative values obtained).
- Report the final mean Kd result, based on the above-described protocols, to 3 decimal points. Report the actual value obtained, even if negative (Note: negative Kd values are undefined, but can occur; large negative values indicate an unacceptably large degree of error within the test).
- Report the estimated Measurement Uncertainty value for the Kd result, as described in section 12.
- If any significant deviations were required from this method, these deviations must be reported.

It is strongly recommended that any sample tested for Kd chloride also be tested for Total Organic Carbon and Soil Texture, as these parameters may show correlations with Kd chloride values.

Performance Requirements

Precision Requirement (of Chloride Method): The analytical method selected for chloride should be sufficiently precise such that the RSD of within-batch sequential chloride measurements of standards or reference materials is less than 5%.

Accuracy Requirement (of Chloride Method): The analytical measurement for chloride should demonstrate recoveries in the range of 90% to 110% on aqueous standards or aqueous reference materials.

Sensitivity Requirement (of Chloride Method): The analytical method selected for chloride measurements must have a detection limit (after accounting for any necessary sample dilutions) of no more than 1 mg/L in the lowest concentration level test samples.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives***
Chloride Method Blank	One per batch	< 2 mg/L
Kd Method Blank	One per batch (1 level)	Kd between -0.10 and 0.10
Chloride Control Std (LCS-Chloride)	One per batch	Within 10% of Target
Chloride Lab Duplicates	One instrumental duplicate per test sample.	5% RPD (based on measured Chloride in solution)
Kd Lab Duplicate	Optional	Not Specified
*Laboratories should report qualified data when any of these DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.		

Chloride Method Blank: Required. Minimum one per Kd test batch. The Chloride Method Blank is prepared by adding 20 mL of deionized water directly to an empty centrifuge tube and carried through the entire process (including filtration steps and any dilution steps).

Chloride Lab Duplicates: Required (Instrumental duplicate only). Minimum one per Kd sample test.

Chloride Control Standard or LCS-Chloride: Required. One per batch. Acts as a second source check on calibration standard accuracy.

Kd Method Blank: Required. Minimum one per Kd test batch. A Kd Method Blank is a complete Kd test, conducted on a suitable negative control sample (Ottawa Sand, 20-30 mesh, e.g. Fisher Scientific S23-3). This inert material is should exhibit a Kd value of zero. To minimize the level of effort, a Kd Method Blank may be conducted using a single chloride concentration level. Using a single concentration level, the Kd Method Blank value should fall within the range of -0.10 to 0.10.

Kd Lab Duplicate: Recommended for crucial test samples. However, the test protocols already include 8 independent Kd measurements for each test sample. The difference between Kd Lab Duplicate results should ideally be less than 0.05 mL/g.

Note: "Soil Blanks" are not related to Kd Method Blanks or Chloride Method Blanks. Soil Blanks are used to determine the amount of chloride contributed to the equilibrated sample solutions by any given soil sample.

Prescribed Elements

This is not a performance based method. All steps must be performed as written.

As a minimum component of laboratory method validation, laboratories must conduct a full Kd Method Blank test (using all 4 concentration levels) on at least one inert solid matrix (e.g. Ottawa Sand), and must achieve a final Kd result of between -0.10 and 0.10. This demonstration of capability must be completed before using the method for environmental samples.

References

Krupka, Kenneth M., Daniel I. Kaplan, Gene Whelan, R. Jeffrey Serne, and Shas V.Mattigod. 1999. Understanding Variation in partition Coefficient, Kd, Values. Vol. 1. The Kd Model, Methods of Measurement, and Application of Chemical Reaction Codes. USEPA, 212 pp. (http://www.epa.gov/radiation/docs/kdreport/vol1/402-r-99-004a.pdf).

Revision History

October 18, 2005:	First draft as BC PBM & version used for validation Round Robin.
February 14, 2006:	Revised based on Round Robin study recommendations. First version of BC Lab Manual Determination of Site-Specific Soil-Water Partitioning Co-efficient (Kd) for Chloride. Effective date for this method is February 14, 2006.

Sodium and Chloride in Soil by Saturated Paste Extraction

Parameters

Water Soluble Sodium (Na)	EMS Code:
Water Soluble Chloride (Cl)	EMS Code:

Analytical Method

Saturated paste soil extraction followed by ionic determination.

Introduction

This method was prepared for the British Columbia Ministry of Water, Land and Air Protection (BCMWLAP), specifically to assess the concentrations of sodium and chloride in soil samples.

Water soluble sodium and chloride are removed from the soil sample using a saturated paste aqueous extraction. Sodium and chloride are determined using analytical techniques appropriate for water samples.

Method Summary

This method involves adding a known quantity of deionized water to a soil sample until saturation is achieved. The sample is allowed to stand for at least 4 hours and the liquid extract is recovered for analysis. Sodium and chloride concentrations in the liquid extract are determined through direct ion measurement techniques.

Supporting test methods are listed in the BCMWLAP *British Columbia Environmental Laboratory Manual*, and include:

1) Saturated Paste Extraction for Soils
2) Sodium, Section C
3) Chloride, Section B

This method is performance-based. Alternate methods for ionic determination may be employed if specified requirements are met.

MDL

Method Detection Limits (MDLs) are dependent on soil textures (saturation percentages), and on the techniques used for sodium and chloride determination in the liquid extract.

Matrix

Soil, solids.

Interferences

Refer to supporting test methods. The interferences encountered will differ depending on the analytical technique used to analyze ionic components in the extract. Analysts should be aware of the limitations of each methodology.

Sample Handling

Refer to supporting test methods.

Apparatus

Refer to supporting test methods.

Reagents

Refer to supporting test methods.

Procedure

1) Refer to the BCMWLAP *British Columbia Environmental Laboratory Manual* method for “Saturated Paste Extraction for Soils”.

2) Methods for determining sodium and chloride concentration in the liquid extract should be based on those listed in the BCMWLAP *British Columbia Environmental Laboratory Manual* or equivalent validated methods. Sodium may be determined by atomic adsorption

spectroscopy, or by atomic emission spectroscopy. Chloride may be determined using ionic chromatography or by colorimetric techniques.

Calculations

Saturated paste ionic components (sodium and chloride) are reported as mg/kg based on a dry sample weight.

$$\text{Saturated Paste Ion Concentration (mg/kg dry weight)} = \frac{C \times (V_1 + V_2)}{W}$$

Where,

C = concentration of ionic component in saturated extract (mg/L)
V_1 = volume of deionized water added to soil aliquot (L)
V_2 = volume of soil moisture in soil aliquot, if any (L)
W = dry weight of soil aliquot (kg)

Use of Alternative Methods

Any analytical method options selected for this analysis must meet or exceed the requirements specified in the *BCMWLAP British Columbia Environmental Laboratory Manual, Section A - Laboratory Quality Assurance / Quality Control Guidelines*. Control limits for precision and accuracy of measurement are at the discretion of the laboratory.

There is provision within the framework of the BC CSR to allow for performance based measures in key areas. It is recognized that the literature contains a variety of predictive equations for the relationship between electrical conductivity and various salt ions in a saturated paste extract. Several jurisdictions also provide remediation guidelines based on measures of electrical conductivity. When compared to direct analysis of sodium and chloride, measurement of electrical conductivity can be more convenient to use (especially in the field), less costly, and in many cases, good correlations exist for certain sites and soil types.

It is required that alternate methods such as electrical conductivity measurement be confidently related to direct ion measurement on a site-specific and soil-type specific basis. This requires that extracts of representative numbers and types of soil samples at a given site be analyzed using direct ion measurement and electrical conductivity procedures, and that a clearly defined mathematical relationship exists.

Those wishing to use alternate techniques to a direct ion measurement must demonstrate this relationship for each major soil type encountered at a given site. As a minimum requirement, at least eight soil samples from each soil type at a given site must be analyzed as a basis for regression analysis. Acceptable alternative methods must achieve a correlation with $R^2 > 0.98$. All equivalence study results must be well-documented and retained by the laboratory and/or CSR practitioner for at least 5 years in the event of audit.

Once an acceptable correlation has been determined, the appropriate correction algorithm must be applied to all subsequent data for the site to convert ionic concentrations to their saturated paste equivalent values.

Laboratories must disclose to their clients, and CSR practitioners must disclose to the ministry where alternative extraction techniques to saturated paste have been employed.

Quality Control

Method Blanks: Analyze at least one with each sample batch.
Duplicates: Analyze at a frequency of approximately 10%, or one per batch.
Spikes or Reference Materials (Post-Prep): Analyze at least one per batch.

References

Carter, Martin R. (Editor), *Soil Sampling and Methods of Analysis, Section 18.2.2 Saturation Extract (Rhoades 1982*), pp. 162-163, Lewis Publishers, Boca Raton, 1993.

Bright, Doug A., and Jan Addison. *Derivation of Matrix Soil Standards for Salt under the British Columbia Contaminated Sites Regulation*. Report to the British Columbia Ministry of Water, Land and Air Protection, Ministry of Transportation and Highways, British Columbia Buildings Corporation and Canadian Association of Petroleum Producers, 2002.

Revision History

March 31, 2005: First Revision

Silica, Reactive, Heteropoly Blue

Parameter Silica, reactive

Analytical Method Automated ascorbic acid reduced heteropoly blue

EMS Code **0120 X338**

Introduction Degradation of silicate rocks results in the presence of silica in natural waters as suspended particles or some form of ion. Due to the tendency of silica to form scale, high levels are of concern in industrial applications.

Method Summary Ammonium molybdate at pH 1.2 reacts with silica to form yellow molybdosilicic acid which is reduced by ascorbic acid to produce an intensely blue heteropoly acid. The absorbance is read at 600 nm.

MDL Typical: 0.5 mg SiO_2/L

Matrix Domestic and industrial wastewaters, natural water, and potable water supplies.

Interferences and Precautions Avoid using glassware and use reagents low in silica. Blanks must be run to correct for any silica introduced to the samples. Tannin, large amounts of iron, colour, turbidity, sulfide and phosphate interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases the interference from tannin. Photometric compensation may be used to cancel interferences from colour and turbidity.

Sample Handling and Preservation 0.5 to 4.5 L plastic bottle.
No preservation, store cool, 4°C.

Stability M. H. T.: 28 days.

Principle or Procedure Autoanalyzer with silica manifold, 600 nm filter and 10mm tubular flow cell. A manual adaptation of this method is also acceptable.

Precision & Accuracy Standard deviation of ±14.3%, relative error of 7.8%, for a synthetic sample containing 5.0 mg SiO_2/L, 10 mg Cl/L, 0.20 mg NH_3-N/L, 1.0 mg NO_3-N/L, 1.5 mg organic N/L, and 10.0 mg PO_4/L in distilled water analyzed by 19 laboratories.

Quality Control Blanks, duplicates, and spikes are run with each set.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-Si F.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Silica, Reactive, Molybdosilicate

Parameter	Silica, reactive
Analytical Method	Automated molybdosilicate
EMS Code	**0120 X339**
Introduction	Degradation of silicate rocks results in the presence of silica in natural waters as suspended particles or some form of ion. Due to the tendency of silica to form scale, high levels are of concern in industrial applications.
Method Summary	Ammonium molybdate at pH 1.2 reacts with silica to form yellow molybdosilicic acid. The absorbance is read at 410 nm.
MDL	Typical: 1 mg SiO_2/L
Matrix	Domestic and industrial wastewaters, natural water, and potable water supplies.
Interferences and Precautions	Avoid using glassware and use reagents low in silica. Blanks must be run to correct for any silica introduced to the samples. Tannin, large amounts of iron, colour, turbidity, sulfide and phosphate interfere. Treatment with oxalic acid eliminates interference from phosphate and decreases the interference from tannin. Photometric compensation may be used to cancel interferences from colour and turbidity.
Sample Handling and Preservation	0.5 to 4.5 L plastic bottle. No preservation, store cool, 4°C.
Stability	M. H. T.: 28 days.
Principle or Procedure	Autoanalyzer with silica manifold, 410 nm filter and 10mm tubular flow cell. A manual adaptation of this method is also acceptable.
Precision & Accuracy	Standard deviation of ±14.3%, relative error of 7.8%, for a synthetic sample containing 5.0 mg SiO_2/L, 10 mg Cl/L, 0.20 mg NH_3-N/L, 1.0 mg NO_3-N/L, 1.5 mg organic N/L, and 10.0 mg PO_4/L in distilled water analyzed by 19 laboratories.
Quality Control	Blanks, duplicates, and spikes are run with each set.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-Si D.
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Sulphate/Sulfate, Automated Colorimetric - MTB

Parameter	Sulfate dissolved (or Sulphate, dissolved)
Analytical Method	Automated methylthymol blue colorimetric
EMS Code	**1121 1400**
Introduction	Sulfate, (SO_4^{2-}), is a naturally occurring ion that may be present over a wide concentration range. The oxidation of pyrite in acid mine drainage may contribute large amounts of SO_4^{2-}. A concern with sulfate arises from the ability of sulfur bacteria to reduce sulfate to sulfide.
Method Summary	After being passed through a cation-exchange column, the sample is reacted with an alcohol solution of barium chloride and methylthymol blue (MTB) at pH 2.5-3.0 to form barium sulfate. The pH of this solution is raised to 12.5-13.0 so that the excess barium reacts with MTB. The uncomplexed MTB is equivalent to the amount of sulfate present.
MDL	Typical: 0.5 mg/L Range: 3-300 mg SO_4/L or 0.5-30 mg SO_4/L
Matrix	Drinking, surface and wastewaters.
Interferences and Precautions	Multivalent cation interferences are eliminated by the ion exchange column. Samples with a pH below 2 should be neutralized since high acid elute concentrations cations from the ion exchange resin. Filter or centrifuge turbid samples.
Sample Handling and Preservation	Plastic or glass (50 mL). No preservation, store cool, 4°C.
Stability	M. H. T.: 28 days.
Principle or Procedure	Autoanalyzer with sulfate manifold, 460 nm interference filters and 15 mm tubular flow cell.
Precision	SD = ± 1.6 at mean concentration of 110 mg $S0_4$/L (26 samples).
Accuracy	Mean recovery = 102% on 24 surface and wastewater samples.
Quality Control	Analyze all working standards in duplicate at beginning of each run to develop a standard curve.

References

a) Methods for the Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 375.2.

b) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-SO_4^{2-} F.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. SEAM MDL deleted. Sulphate synonym added.

Sulphate/Sulfate, Gravimetric

Parameter Sulfate, dissolved (or Sulphate, dissolved)

Analytical Method Barium chloride gravimetric

EMS Code **1121 X061**

Introduction Sulfate is widely distributed in nature and normally found in water as a result of degradation of sulfate-containing rock.

Method Summary Sulfate is precipitated as barium sulfate ($BaSO_4$) in HCl medium by the addition of barium chloride. After the digestion period, the precipitate is filtered, washed with hot water until chloride free, ignited and weighed as $BaSO_4$.

MDL Typical: 1 mg SO_4/L

Matrix Drinking, surface and saline waters, wastewater.

Interferences and Precautions High results may be obtained for samples containing suspended matter, nitrate, sulfite and silica. Alkali metal sulfates frequently yield low results. This is especially true of alkali hydrogen sulfates. Heavy metals such as chromium and iron can interfere. Do not let the filter paper flame during the ashing of the precipitate.

Sample Handling and Preservation Plastic or glass (50 mL).
Cool, 4°C.

Stability M. H. T.: 28 days.

Principle or Procedure Steam bath. Drying oven. Muffle furnace. Analytical balance. Filter paper, ashless fine (Whatman 42 or equivalent).

Precision SD = ± 4.7% at 259 mg SO_4/L (aqueous mix of 9 ions).

Accuracy Relative error = 1.9% at 259 mg SO_4/L (aq. mix of 9 ions).

Quality Control None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-SO_4 C.

b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983, Method 375.3.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sulphate synonym added.

Sulphate/Sulfate, Ion Chromatography

Parameter	Sulfate, dissolved (or Sulphate, dissolved)
Analytical Method	Ion chromatography
EMS Code	**1121 X044**
Introduction	Sulfate is widely distributed in nature and normally found in water as a result of degradation of sulfate-containing rock.
Method Summary	A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector.
MDL	Typical: 0.02 mg SO_4/L Range: 1-100 mg SO_4/L
Matrix	Drinking and surface waters. Mixed wastewater.
Interferences and Precautions	Interferences can be caused by substances with retention times similar to and overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Method interference can be caused by reagent or equipment contamination.
Sample Handling and Preservation	Plastic or glass (50 mL). No preservation, store cool, 4°C.
Stability	M. H. T.: 28 days.
Principle or Procedure	Ion chromatograph configured with guard, separator and suppressor columns and equipped with a conductivity detector.
Precision	SD = ± 1.47 mg/L at 98.5 mg SO_4/L (drinking water).
Accuracy	104% at 98.5 mg SO_4/L (drinking water).
Quality Control	The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing lab performance. Field and laboratory duplicates should be analyzed. Measure retention times of standards. Second order calibration may be required for sulphate above 100 mg SO_4/L.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4110.
b) EPA-600/4-84-017, Test Method, Technical Addition to Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), USEPA, Revised March 1983, Method 300.0.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sulphate synonym added.

Sulphate/Sulfate, Turbidimetric

Parameter
Sulfate, dissolved (or Sulphate, dissolved)

Analytical Method
Barium sulfate turbidimetric

EMS Code
1121 X064

Introduction
Sulfate is widely distributed in nature and normally found in water as a result of degradation of sulfate-containing rock.

Method Summary
Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined using a nephelometer or spectrophotometer and compared to a curve prepared from standard sulfate solutions.

MDL
Typical: 1.0 mg $S0_4$/L
Range: 1-40 mg $S0_4$/L

Matrix
Drinking and surface waters, wastewater.

Interferences and Precautions
Suspended matter and colour interfere, although colour interference is less than for the colorimetric sulfate procedure. Silica in concentrations over 500 mg/L will interfere.

Sample Handling and Preservation
Plastic or glass (50 mL).
No preservation, store cool, 4°C.

Stability
M. H. T.: 28 days.

Principle or Procedure
Nephelometer or spectrophotometer at 420 nm with a light path of 4-5 cm. An automated version of this technique is also available.

Precision
SD = ± 7.86 mg/L at 110 mg SO_4/L.

Accuracy
As bias, -3.3 mg/L at 110 mg SO_4/L.

Quality Control
Correct for sample colour and turbidity by running blanks from which barium chloride has been omitted. Suitable for all ranges of sulfate, but use sample aliquot with not more than 40 mg SO_4/L. Above 50 mg/L the accuracy decreases and suspensions lose stability.

References
a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-$S0_4$ E.
b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983, Method 375.4.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sulphate synonym added.

Sulfide in Waters by Colorimetric Analysis – PBM

Parameters

Sulfide (as H_2S)

Sulfide, Dissolved

Analytical Method

Sulfide precipitated with zinc acetate under basic conditions is determined colorimetrically as methylene blue, formed from the reaction of zinc sulfide under acidic conditions with N,N-dimethyl-p-phenylenediamine and ferric chloride.

Introduction

This method is applicable to the quantitative determination of sulfide in water. Sulfide, commonly found in ground water, is often formed by bacterial reduction of sulfate in rocks and ores and from decomposition of organic matter. Gaseous hydrogen sulfide has an unpleasant smell and is highly toxic to humans, acting as a chemical asphyxiant. Dissolved sulfide is toxic to fish and other aquatic organisms. Sulfide attacks metals directly, forming metal sulfides. Highly corrosive sulfuric acid may be formed from biological oxidation of sulfide, and will attack concrete sewer pipes.

Sulfide (as H_2S) is the parameter that is applicable to Schedule 6 of the BC CSR.

Method Summary

Zinc sulfide precipitate in deionized water is dissolved in acidified N,N-dimethyl-p-phenylenediamine solution. This solution is reacted with ferric chloride to form methylene blue. Diammonium hydrogen phosphate is added to remove the colour associated with ferric chloride and the intensity of the methylene blue is read colorimetrically at 664 nm. Results for each sample are calculated from a calibration curve. This test method is applicable to manual or automated analysis procedures.

Parameter Applicability, MDLs

The MDLs listed below are achievable for this method in a typical laboratory environment. Ensure that the detection limits reported by the laboratory are sufficient to meet any applicable regulatory standards.

Parameter	Approximate MDL (mg/L)	EMS Code
Sulfide (as H_2S)	0.002 – 0.020	0125LLHS
Sulfide, Dissolved	0.002 – 0.020	n/a

Matrix

Ground water, waste water.

Interferences and Precautions

Strong reducing agents such as sulfite and thiosulfate at concentrations above 10 mg/L may prevent colour formation.

Iodide at concentrations greater than 2 mg/L may diminish colour formation.

Extremely high sulfide concentrations may completely inhibit the reaction, causing the solution to turn pink instead of the expected blue. Such samples will require dilution before the addition of reagents.

Ferrocyanide also produces a blue colour, which is removed by adding diammonium hydrogen phosphate.

Sulfide is highly reactive, and is rapidly oxidized by dissolved oxygen (usually to thiosulfate or sulfate, sometimes to sulfur), especially when exposed to light or in the presence of heavy metals. Sulfide oxidation may be minimized through the use of nitrogen purged reagent water (for standards or dilutions), and by the use of ascorbic acid as an anti-oxidant.

Sodium hydrosulfite will release sulfide when the sample is acidified.

Many metals such as Hg, Cd and Cu can form insoluble sulfides which may cause low recoveries.

Sample Handling, Preservation and Hold Time Requirements

Parameter	Sample Container	Storage Temp.*	Preservation	Holding Time	References
Sulfide (as H_2S)	Plastic or Glass	≤6°C	Field Preserve within 15 minutes of sampling w/ ZnAc/NaOH to pH >9 as per APHA 4500 S^{2-}	7 days	APHA 4500 S^{2-}, APHA 1060
Sulfide, Dissolved	Plastic or Glass	≤6°C	Flocculate within 15 minutes of sampling, then preserve immediately with ZnAc/NaOH as above	7 days	APHA 4500 S^{2-}, APHA 1060

*Storage temperature applies to storage at the laboratory. Samples should be packed with ice or cold packs to maintain a temperature of ≤10°C during transport to the laboratory. To prevent breakage, water samples stored in glass should not be frozen.

Analytical Procedure

Reagents:

a) N,N-dimethyl-p-phenylenediamine oxalate $(CH_3)_2NC_6H_4NH_2]_2{\cdot}H_2C_2O_4$, CAS # 62778-12-5

b) Sulfuric acid (H_2SO_4)

c) Amine-Sulfuric Acid Stock Solution 1:1 H_2SO_4

d) Ferric chloride ($FeCl_3{\cdot}6H_2O$)

e) Diammonium hydrogen phosphate $(NH_4)_2HPO_4$

f) Zinc acetate $(Zn(C_2H_3O_2)_2{\cdot}(H_2O)_2)$

g) Sodium hydroxide (NaOH)

h) Sodium sulfide ($Na_2S{\cdot}9H_2O$)

i) 0.025 N Potassium iodide (KI)

j) Concentrated hydrochloric acid (HCl)

k) 0.100 N Sodium thiosulfate ($Na_2S_2O_3$)

l) Starch solution

m) Type II Deionized water which is < 1 µS/cm at 25°C.

n) Aluminum chloride solution, $AlCl_3$•6H2O, ~ 2M, dissolve 100 g into 114 mL deionized water or equivalent (required for dissolved sulfide only).

Detailed procedures are not provided in this method. Refer to Standard Methods for the Examination of Water and Wastewater, America Public Health Association, Washington DC, 2000, Method 4500-S2−D Methylene Blue Method or 4500-S2−E Gas Dialysis, Automated Methylene Blue Method.

Samples for sulfide analysis must be preserved in the field within 15 minutes of sampling (or analyzed in the field). Samples that arrive unpreserved at the laboratory should be considered compromised. If analyzed at all, sulfide results for such samples must be qualified as unreliable.

All samples should be visually assessed for colour. Coloured samples may require the sample concentration procedure to remove colorimetric interferences.

If sample concentration of a preserved sample is required, either to achieve lower detection limits or to remove interferences, first check pH and add additional NaOH if necessary to increase pH to ≥ 9. Centrifuge or allow the zinc sulfide precipitate to settle, and replace the supernatant with an appropriate volume of deionized nitrogen-purged water.

Analysis of dissolved sulfide requires the use of an aluminum hydroxide flocculation procedure, which must be conducted within 15 minutes of sampling. Follow instructions from APHA 4500 $S2^-$ B, Separation of Soluble and Insoluble Sulfides. Allow sample to

stand for 5 to 15 minutes, then decant clear supernatant to sampling container and preserve immediately with zinc acetate and NaOH (or analyze immediately).

Stock sulfide standards must be prepared and verified daily using the iodometric method outlined in SM 4500-F. Alternatively, commercially prepared single-use certified reference standards may be used.

Acid-dissociable sulfides are converted to H_2S by the addition of N,N-dimethyl-p-phenylenediamine prepared with H_2SO_4. The solution is reacted with ferric chloride solution to produce methylene blue. After colour formation, diammonium hydrogen phosphate is added to remove the colour associated with ferric chloride.

The intensity of the methylene blue is read colorimetrically at 664 nm. The concentration of hydrogen sulfide is calculated from a calibration curve prepared at known sulfide concentrations that bracket the working range of the method.

For CSR Schedule 6 applications, multiply sulfide [S^{2-}] concentrations by 1.063 to convert to "as H_2S" concentrations (1.063 is the molecular weight ratio of H_2S / S), and report "Sulfide (as H_2S)".

Performance Requirements

Any analytical method options selected for this analysis must meet or exceed the method validation performance requirements specified below:

Accuracy and Precision requirements apply to measures of long-term method performance (averages and standard deviations). Achievement of these requirements is to be demonstrated during initial and ongoing method re-validation studies. They do not constitute acceptance criteria or Data Quality Objectives for individual Quality Control samples.

For Initial Validations, averages of at least 8 Laboratory Control Samples or Reference Materials (RMs) must be assessed (preferably taken from multiple analytical batches).

Ongoing Re-validations (performance reviews) should assess QC data encompassing longer timeframes (e.g. a minimum of 6 months, preferably 1 year). A minimum frequency of 2 years is recommended for Ongoing Re-validations.

Accuracy Requirement: Laboratories must demonstrate method accuracy (measured as average recovery) through repeat analysis of Laboratory Control Samples or Reference Materials at concentrations above ten times the MDL. Average recovery must be between 85-115%.

Precision Requirement: Laboratories must demonstrate method precision through repeat analysis of Laboratory Control Samples or Reference Materials at concentrations above ten times the MDL. Precision measured as % relative standard deviation (RSD) must be <15%.

Sensitivity Requirement: Where possible, the method should generate Method Detection Limits that are less than 1/5 of applicable numerical standards. The method is not fit-for-purpose if an MDL exceeds a guideline, standard, or regulatory criteria against which it will be used for evaluation of compliance.

Linear Dynamic Range (LDR): A linear calibration must be used for this test. Linear range studies are to be performed during the initial validation of the method to determine the upper limit of linearity. The LDR should be determined by analyzing at least 3 different standard concentrations and the observed analyte concentration at all levels must lie within 90-110% of the nominal concentration of the standard. Note that the LDR concentration may not be the upper limit of the element, but rather the upper concentration examined. If a sample concentration exceeds the LDR, it must be diluted and reanalysed.

Quality Control

Summary of QC Requirements		
QC Component	**Minimum Frequency**	**Minimum Data Quality Objectives* (DQO)**
Method Blank	1 per 20 samples	Less than reported DL
Laboratory Duplicates	1 per 20 samples	≤ 20% RPD
Laboratory Control Sample or Reference Material	1 per 20 samples	75–125% recovery
Control Standard / Initial Calibration Verification (ICV)	1 per analysis batch	85-115% recovery
Continuing Calibration Verification (CCV)	1 per 20 samples and at the end of each run	80-120% recovery for mid-level standards

* Minimum DQOs apply to individual QC samples, not averages, at levels above 10x MDL. Laboratories should report qualified data when DQOs are not met, unless other evidence demonstrates that the quality of associated sample data has not been adversely affected.

QC Details

Method Blanks, Laboratory Control Samples, and Reference Materials must be prepared using zinc acetate / NaOH preservative so that they will be representative of test samples.

Control Standard / Initial Calibration Verification must be from a source that is independent from calibration standards. Control Standards may also be used as Continuing Calibration Verifications (CCV's).

Prescribed Elements

The following components of this method are mandatory:

a) Sample holding times and preservation requirements must be adhered to. Field preservation or field analysis is required. Samples analyzed beyond the stated holding time must be qualified.

b) All performance requirements and Quality Control requirements must be met.

c) Sulfide stock must be standardized daily to establish a known concentration of sulfide. Alternatively, commercially prepared single-use reference standards may be used. Working standards are prepared at nominal concentrations from standardized or commercial reference source stocks.

d) Samples without colour reagent must be used to establish background colour, as per the Tube A / Tube B procedure from APHA 4500 S2- Method D. B samples do not contain N, N-dimethyl-p-phenylenediamine oxalate and act as background colour correction when the B result is subtracted from the A result. This procedure is not applicable or required when APHA Method E is utilized, whereby a gas dialysis membrane is used to isolate H_2S.

e) Automated test methods for sulfide must incorporate adequate stirring mechanisms to ensure homogeneous distribution of zinc sulfide precipitate during instrumental sub-sampling.

f) Samples to be analyzed for dissolved sulfide (not intended for CSR purposes) must be flocculated within 15 minutes of sampling using aluminum chloride and NaOH as per APHA Method 4500 S2- Method B, followed by immediate preservation with zinc acetate / NaOH.

References

Standard Methods for the Examination of Water and Wastewater, America Public Health Association, Washington DC, 2000, Method 4500-$S2^-$ D or Method 4500-S^{2-} E.

Revision History

October 1, 2013: First version of BC Lab Manual sulfide method in PBM format. Effective date for this method is October 1, 2013.

Sulphide/Sulfide by Silver/Sulfide Electrode

Parameter Sulfide, total (or Sulphide, total)

Analytical Method Silver/sulfide ion selective electrode

EMS Code **0125 X340**

Introduction The presence of sulfide in water as hydrogen sulfide or bisulfide results in disagreeable tastes and odours. Sulfide is often present in groundwater associated with sulfide rocks and ores and with hot springs. In wastewaters, sulfide results from the decomposition of organic matter, from industrial wastes or from the bacterial reduction of sulfate. In clean water, sulfide odour can be detected between 0.085 and 0.25 µg/L. The Canadian Drinking Water Aesthetic Objective Guideline is 0.05 mg/L. Fish hatcheries require a limit of 0.002 mg/L.

Method Summary The silver/sulfide electrode includes a sensing element bonded into an epoxy body. When this sensing element is in contact with a solution containing sulfide or silver ions, an electrode potential develops across the sensing element. The sensing element will respond to both silver ions and sulfide ions but since both ions cannot exist in solution together because of the extreme insolubility of silver sulfide, the electrode can be used to determine silver or sulfide. The potential, measured against a constant reference potential, is proportional to the concentration of free sulfide (or silver) ions in solution.

MDL Typical: 0.05 mg/L
Range: Below 1 mg/L

Matrix Fresh water, marine water, process waters and effluents.

Interferences and Precautions

a) Mercury will affect electrode response; however, in a sulfide sample, HgS and Hg_2S are so insoluble that both mercury and sulfide will not usually be found in solution.

b) When analyzing standards, check previous millivolt readings for the same standard - there should be little or no change. Samples suspected of containing no sulfide can be analyzed prior to standardization to see if there is any electrode response at all.

c) Stabilization time for the first measurement could be as long as 5 minutes. Subsequent measurements should not require such a long stabilization time.

d) If possible, determine low sulfide concentration samples first since the probe responds more quickly when changing from a low concentration to a higher concentration.

e) Rinse the probe between readings with 0.1N NaOH then wipe dry. Do not use deionized water.

Sample Handling and Preservation

Collect at least 100 mL of sample in a clean plastic bottle. Minimize aeration during collection and fill the bottle to the top to prevent the volatilization and/or oxidation of sulfides. Samples are preserved with 2 mL 2N $Zn(CH_3C00)_2$/L.

Stability

Sulfides are precipitated as ZnS which prevents volatilization and prevents further sulfide generation. Preserved samples can be stored for up to 7 days.

Principle or Procedure

For method details, see references [a] and [b].

Precision

Factors such as temperature, drift and noise affect precision. With frequent calibration, direct electrode measurements are reproducible to ±4% to 5% [b].

Accuracy

None listed.

Quality Control

Standard reference materials (SRM's) for sulfide are not available at this time. Match standards and samples as closely as possible to control variables such as temperature and pH.

References

a) Environment Canada, Conservation and Protection, Pacific and Yukon Region Laboratory Manual, Sulfides - Specific Ion Probe, Version 1.0, (1987).

b) Orion Research, Model 95-18 Silver/Sulfide Electrode Instruction Manual, Rev. B, (1991).

c) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 4500-S^{2-} A.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Sulphide synonym added.

Surfactants, Anionic as MBAS

Parameter Surfactants, anionic (methylene blue active)

Analytical Method Methylene blue, colorimetric

EMS Code **0122 X341**

Introduction Methylene blue active substances (MBAS) promote the extraction of methylene blue, a cationic dye, from an aqueous solution into an immiscible organic liquid. This occurs through ion-pair formation by the MBAS anion and the methylene blue cation. The intensity of the resulting blue colour in the organic phase is a measure of MBAS. Linear alkylbenzene sulfonate (LAS) is the most widely used anionic surfactant and is used to standardize the MBAS method.

Method Summary The sample, made just acid to phenolphthalein and treated with an excess of methylene blue, is extracted three times with chloroform ($CHCl_3$). The combined chloroform extracts are washed with acidic buffer solution, dried and made to volume for colorimetric measurement at 652 nm.

MDL Typical: 0.025 mg MBAS/L as LAS
Range: 0.025 - 0.5 mg/L LAS

Matrix Waters and wastewater.

Interferences and Precautions

Positive interferences result from all other MBAS species present. If a direct determination of any individual MBAS species, such as LAS, is sought, all others interfere. Substances such as organic sulfonates, sulfates, carboxylates and phenols, and inorganic thiocyanates, cyanates, nitrates, and chlorides also may transfer more or less methylene blue into the chloroform phase. Negative interferences can result from the presence of cationic surfactants and other cationic materials, such as amines, because they compete with the methylene blue in the formation of ion-pairs. Particulate matter may give negative interferences through absorption of MBAS. Because of the inherent properties of surfactants, special analytical precautions are necessary. Foam on the sample surface indicates that the surfactants are distributed between the air phase and the associated bulk aqueous phase and surfactant concentration in the latter may be significantly depleted.

If foam has formed, let it subside by standing, or collapse it by other appropriate means, and remix the liquid phase before sampling. Adsorption of surfactant from aqueous solutions onto the walls of the container, when concentrations below about 1 mg/L are present, may seriously deplete the bulk aqueous phase. Minimize adsorption errors, if necessary, by rinsing the container with the sample, and for anionic surfactants, by adding alkali phosphate (e.g., 0.03 N KH_2PO_4).

Sample Handling and Preservation Plastic or glass, 250mL to 4.5 L.
Unfiltered, no preservation.

Stability M. H. T.: 28 days.

Principle or Procedure Anionic surfactants form ion-pairs with methylene blue which are extractable from aqueous solution into an immiscible organic solvent. Absorbance of the extraction solvent at 652 nm is proportional to the concentration of surfactants in the sample.

Precision and Accuracy A synthetic sample containing 270 µg LAS/L in distilled water was analyzed in 110 laboratories with a relative standard deviation of ±14.8% and a relative error of 10.6%. A tap water sample to which was added 480 µg LAS/L was analyzed in 110 laboratories with a relative standard deviation of ±9.9% and a relative error of 1.3%. A river water sample with 2.94 mg LAS/L added was analyzed in 110 laboratories with a relative standard deviation of ±9.1% and a relative error of 1.4%.

Quality Control None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA & WEF, 18th Edition, 1992, Method 5540 C.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Surfactants, Sublation Extraction

Parameter Surfactants

Analytical Method Sublation extraction

EMS Code **0122 X342**

Introduction Surfactants, which combine in a single molecule a strongly hydrophobic group with a strongly hydrophillic one, enter water and wastewaters mainly by discharge of aqueous wastes from household and industrial laundering and other cleansing operations. Such molecules tend to congregate at the interfaces between the aqueous medium and the other phases of the system such as air, oily liquids, and particles, thus conferring properties such as foaming, emulsification and particle suspension. The sublation process isolates the surfactant, regardless of type, from dilute aqueous solution and yields a dried residue relatively free of nonsurfactant substances.

Method Summary A stream of nitrogen is bubbled up through a vertical column containing the sample and an overlaying layer of ethyl acetate. The surfactant is absorbed at the water - gas interfaces of the bubbles and is carried into the ethyl acetate layer. The bubbles escape into the atmosphere leaving behind the surfactant dissolved in ethyl acetate. The solvent is separated, dehydrated, and evaporated, leaving the surfactant as a residue suitable for methylene blue analysis, free of interferences.

MDL Range: Below 1 mg/L

Matrix Waters and wastewaters.

Interferences and Precautions The sublation method is specific for surfactants, because any substance preferentially absorbed at the water-gas interface is by definition a surfactant. The sublation process separates only dissolved surfactants. If particulate matter is present it holds back an equilibrium amount of absorbed surfactant.

Sample Handling and Preservation Plastic or glass (1 L).
No preservation required.

Stability M. H. T.: 28 days.

Principle or Procedure The surfactant is absorbed at the water - gas interfaces of the nitrogen bubbles and is carried into the ethyl acetate layer.

Precision ± 7.4 % (n = 100).

Accuracy Average recovery 90 - 98%.

Quality Control None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA & WEF, 18th Edition, 1992. Method 5540 B.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Tannin and Lignin

Parameter Tannin and lignin

Analytical Method Heteropoly acid

EMS Code

a)	Manual	**0123 X120**
b)	Automated	**0123 0951**

Introduction Lignin is a plant constituent that often is discharged as a waste during the manufacture of paper pulp. Another plant constituent, tannin, may enter the water supply through the process of vegetable matter degradation or through the wastes of the tanning industry. Tannin also is applied in the so-called internal treatment of boiler waters, where it reduces scale formation by causing the production of a more easily handled sludge.

Method Summary Aliquots of sample are reacted with Folin phenol reagent (a mixture of tungstic and molybdic acids) and, after time for reaction, with carbonate solution. The absorbance of the developed colour is measured at 700 nm using a spectro-photometer equipped with 1 cm cells. It should be emphasized that the reaction is not specific for lignin or tannin.

MDL Typical: Approximately 0.025 mg/L for phenol and tannic acid and 0.1 mg/L for lignin with a 1-cm-path-length spectrophotometer.
Range: 0.1 mg/L - 9 mg/L.

Matrix Waters and wastewaters.

Interferences and Precautions Other substances able to reduce Folin phenol reagent will produce a false positive response. Organic chemicals known to interfere include hydroxylated aromatics, proteins, humic substances, nucleic acid bases, fructose, and amines. Inorganic substances known to interfere include iron (II), manganese (II), nitrite, cyanide, bisulfite, sulfite, sulfide, hydrazine, and hydroxylamine hydrochloride. Both 2 mg ferrous iron/L and 125mg sodium sulfite/L individually produce a colour equivalent to 1 mg tannic acid/L. If the identity of the compound in the water sample is not known, use phenol and report results as "substances reducing Folin phenol reagent" in mg phenol/L. Interpret such results with caution.

Sample Handling and Preservation Plastic or glass (50 mL).
No preservation, store cool, 4°C.

Stability M. H. T.: 28 days.

Principle or Procedure Aromatic hydroxyl groups in lignin and tannin react with Folin phenol reagent (tungstophosphoric and molybdophosphoric acids) to produce a blue colour suitable for estimation of concentrations up to at least 9 mg/L.

Precision ± 7% for 0.1 mg/L.

Accuracy Recovery = 107%.

Quality Control None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition, 1992. Method 5550 B.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Thiocyanate, Ion Chromatography

Parameter	Thiocyanate
Analytical Method	Ion chromatographic analysis
EMS Code	**THIO X044**
Introduction	Thiocyanate (SCN^-) is of concern because, when wastewater containing it is chlorinated, highly toxic cyanogen chloride is produced.
Method Summary	A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressor column and conductivity detector.
MDL	Typical: 0.05 mg SCN^-/L Range: 0.05 to 2.0 mg SCN^-/L
Matrix	Fresh water and wastewaters.
Interferences and Precautions	Interference can be caused by substances with retention times similar to and overlapping those of the ion of interest. Large amounts of an anion can interfere with peak resolution of an adjacent anion. Method interference can be caused by reagent or equipment contamination. Industrial waste may contain unknown interferences.
Sample Handling and Preservation	Plastic or glass (50 mL). Add NaOH to pH >12.
Stability	M. H. T.: 14 days.
Principle or Procedure	Ion chromatograph. Guard, separator and suppressor columns, conductivity detector.
Precision	None listed.
Accuracy	None listed.
Quality Control	The laboratory should spike and analyze a minimum of 10% of all samples to monitor continuing lab performance. Field and laboratory duplicates should be analyzed. Measure retention times of standards.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4110 B (for the general ion chromatographic technique -not specifically for thiocyanate).

b) EPA-600/4-84-017, Test Method Technical Addition to Methods for Chemical Analysis of Water and Wastes (EPA-600/4-79-020), USEPA, Revised March 1983, Method 300.0 (for the general ion chromatographic technique -not specifically for thiocyanate).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes.

Turbidity, Nephelometric

Parameter	Turbidity
Analytical Method	Nephelometric
EMS Code	**0015 1140**
Introduction	Turbidity measurements within water provide insight into its clarity. Turbidity is normally caused by suspended matter such as clay, plankton or silt.
Method Summary	The light, scattered at right angles to the incident light by the sample under defined conditions, is measured in a nephelometer and compared with the effect produced by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity.
MDL	Typical: 0.1 Nephelometric turbidity unit (NTU) Range: 0 to 40 NTU
Matrix	Drinking, surface and saline waters.
Interferences and Precautions	Presence of floating debris and coarse sediments which settle out rapidly will give low readings. Fine air bubbles will affect results in a positive manner. The presence of true colour, or dissolved substances which absorb light, will result in low turbidities.
Sample Handling and Preservation	Plastic or glass (100 mL). No preservation, store cool, 4°C.
Stability	M. H. T.: 28 days.
Principle or Procedure	Nephelometer (with light source) and one or more photoelectric detectors.
Precision	SD = ± 0.60 and 1.2 units at NTU levels of 26 and 75.
Accuracy	None listed.
Quality Control	Use turbidity-free water for blanks and dilution. Sample tubes must be clear, colourless glass.
References	a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 2130 B. b) Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, USEPA, Revised March 1983. Method 180.1
Revision History	February 14, 1994: Publication in 1994 Laboratory Manual. December 31, 2000: SEAM codes replaced by EMS codes.

Appendix 1

Table 1: Method Sensitivity

Reference pH	N	% Sensitivity Mean	% Sensitivity Std Dev	% Sensitivity CONTROL LIMITS Lower	Upper
4.00 to 10.00	109	98.80	0.52	94.12	103.48

Table 2: Method Blank

	N	Expected pH pH Units	Measured pH pH Units	Std. Dev.	Control Limits
Blank	316	N/A	6.16	0.17	± 0.50

Most data from the blanks run at Env. Canada (PESC) prior to May 1999.

Table 3: Method Bias

Certified value / pH units	N	Measured pH mean	Std. Dev.	% Bias	Significant (95% CL)
{**a**} 9.08 ± 0.20	3	9.031	0.011	- 0.54	No
{**b**} 6.97 ± 0.03	6	6.922	0.005	- 0.69	No
{**c**} 9.05 ± 0.20	5	9.022	0.021	- 0.31	No

Most data from the certified reference solutions run at Env. Canada (PESC) prior to May 1999.
{**a**} pH standard by Environmental Resource Associates. Lot #9967.
{**b**} Low Ionic Strength pH buffers by Orion Research. Lot #YX1.
{**c**} pH standard by Environmental Resource Associates. Lot #9964.
CL- Confidence Limit.

Table 4: Single Analyst Method Precision

Sample Type	N	pH Mean	Std Dev	% RSD
Mine Effluent	5	7.53	0.012	0.16
Sewage Effluent	5	3.57	0.140	3.91
River Water	5	7.90	0.051	0.64
Ground Water	5	8.16	0.009	0.11

Most data from the samples run at Env. Canada (PESC) prior to May 1999.

Table 5: Single Analyst (Within-Run) Precision

pH Analytical Range / pH units	No. of Sets of Duplicates	%Mean Normalized Range	Std. Dev.	CONTROL LIMITS for Normalized Duplicate Range
0 - 14	302	0.320	0.456	1.37

Most data from the duplicates run at Env. Canada (PESC) prior to May 1999.

Table 6: Control Sample Bias (Data Current to May 1999)

Reference pH	N	% Recovery Mean	% Recovery Std Dev	% Recovery CONTROL LIMITS Lower	Upper
4.00 to 10.00	315	100.06	0.278	99.11	101.43
8.78	35	99.92	0.67	97.91	101.93

Appendix 2

Table 1: Ministry Preferred DQO's

Sample Type	Range	Bias (pH Units)	Precision (pH Units)
Effluent	0-14	0.1	± 0.1
Freshwater	0-14	0.05	± 0.05
Marine	0-14	0.05	± 0.05
Precipitation (rain)	0-14	0.01	± 0.01