Section B

PHYSICAL, INORGANIC AND MISCELLANEOUS CONSTITUENTS

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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.

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.

Chlorine, Total Residual, DPD Colorimetric

Parameter

Chlorine, total residual

Analytical Method

DPD colorimetric

EMS Code

1016 X103

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. The N,N-diethyl-p-phenylenediamine (DPD) colorimetric method is applicable to the matrices listed.

Method Summary

Liberated iodine reacts with DPD to produce a red solution which is measured spectrophotometrically.

MDL

Typical: 0.2 mg Cl_2/L
Range: 0. 2-4.0 mg Cl_2/L

Matrix

Natural and treated waters

Interferences and Precautions

Any oxidizing agents; these are usually present at insignificant concentrations compared to the residual chlorine. Turbidity and colour will essentially prevent the colorimetric analysis. Distilled water used for dilution should be checked for chlorine demand.

Sample Handling and Preservation

Plastic or glass (200mL). No preservation required.

Stability

Analyze immediately

Principle or Procedure

Spectrophotometer. 515 nm. Cells of light path 1 cm or longer.

Precision

SD = ± 27.6% at 0.66 mg Cl/L

Accuracy

Relative error = 15.6% at 0.66 mg Cl/L

Quality Control

None listed.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992, Method 4500-Cl_2 D.

b) Methods for Chemical Analysis of Water and Wastes EPA-600/4-79-020, USEPA, Revised March 1983, Method 330.5

Revision History

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

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, Single Wavelength

Parameter

Colour, single wavelength, dissolved

Analytical Method

Spectrophotometer - single wavelength (400nm)

EMS Code

a) No pH adjustment **1052 1320**
b) pH adjusted to 7.6 **1052 X497**

Introduction

Colour in water may result from the presence of natural metallic ions, humus, peat materials, plankton, weeds, and industrial waste. The single wavelength spectrophotometric colour procedure is a variation on the visual colour comparison procedure that provides an objective and more precise measure of sample colour. 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 ration 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.

Method Summary

Colour is determined by spectrophotometric comparison of the sample, at a specific wavelength, with known concentrations of coloured solutions. The sample is either adjusted to pH 7.6 (and the colour reported as such) or the pH of the sample is determined and reported as well.

MDL

Typical: 5 SWL 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 determined. 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
No preservation, store cool, 4°C

Stability

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

Procedure:
Apparatus

a) UV/VIS spectrophotometer
b) 5 cm cell

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

1) 50 colour units: Dilute stock standard 1:9 with deionized water.
2) 10 colour units: Dilute stock standard 1:49 with deionized water.

Procedure

a) Calibrate the spectrophotometer using the two working standards at a wavelength of 400 nm, using a 5cm cell.

b) Using un-shaken sample, decant into the 5 cm cell, and record the value in colour units as generated by the spectorophotometer.

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 A (for an overview on colour).

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Out of print reference deleted.

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) SelectF1 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 te cell with D1 and scan as though it were a sample. This is a check on technique and clarity of te 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 te 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 un-shaken 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 $1^1/_4$ 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; Weak Acid Dissociable (Zinc Acetate Distillation)

Parameter Cyanide; weak acid dissociable

Analytical Method Zinc acetate dist.; isonicotinic - barbituric acid colorimetric

EMS Code
a) WAD Cyanide (water), units = mg/L **0157 X323**
b) WAD Cyanide (soil), units = µg/g **0157 X496**

Introduction 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 degree of dissociation of these complexes, analytical methods that distinguish between readily available and more stable forms of cyanide are appropriate. Weak acid dissociable cyanide appears to correlate well with cyanide amenable to chlorination.

Method Summary In this procedure a weak acid [$(CH_3COO)_2Zn.2H_2O$] reflux distillation is carried out to liberate hydrogen cyanide (HCN) from simple cyanides. The resulting HCN is distilled from the digestion mixture and trapped in a weak NaOH solution. This basic solution is then analyzed colorimetrically (See Cyanide -Colorimetric Isonicotinic-Barbituric Acid Method.)

MDL Typical: 0.005 mg/L CN/L

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, however, analysis within 7 days is recommended.

Principle HCN is generated from simple cyanides and complex cyanides that dissociate under the conditions of the digestion process. The HCN is distilled into an alkaline trapping solution from which aliquots are taken for colorimetric analysis.

Procedure

Reagents for Distillation

a) Acetic Acid (1 to 9):

Mix 1 volume glacial acetic acid with 9 volumes distilled water.

b) Acetate Buffer:

Dissolve 410 g sodium acetate trihydrate ($NaCH_3COO \cdot 3H_2O$) in 500mL of distilled water. Adjust pH to 4.5 by the addition of 1 to 9 acetic acid. Bulk to one litre.

c) Zinc Acetate:

Dissolve 100g zinc acetate dihydrate [$(CH_3.COO)_2 Zn \cdot 2H_2O$] in one litre of distilled water.

Procedure

a) Refer to the cyanide, strong acid dissociable, distillation procedure. Follow steps 1, 2, 4, and 5. (See Note 1).

b) Add 10 mL of acetate buffer and 10 mL of zinc acetate solution through the thistle tube and rinse with distilled water.

c) Continue as with the cyanide, strong acid dissociable, distillation procedure, from Step 7.

Note:

1. No $CdCl_2$ is required for WAD-CN.

References

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

Revision History

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

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.

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.

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.
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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

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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, NO_3 + NO_2, 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-NO_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.
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Nitrogen, NO_3 + NO_2, 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

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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

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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

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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 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 unit

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

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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.

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 turbiditymust 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), 0.45 µm

Parameter	Residue, filterable
Analytical Method	Gravimetric, 0.45 µm filter, 180°C
EMS Code	**0007 X026**
Introduction	Filterable residue (FR), also referred to as total dissolved solids (TDS), represents the portion of the water that will pass through a filter of a particular size. A pore size of 0.45 µm is generally considered the dividing line between microscopic particulate and dissolved material. The final result provides a measure of the dissolved mineralization in the water.
Method Summary	A well-mixed sample is filtered through a standard membrane 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) Store cool, 4°C
Stability	M. H. T.: 14 days
Principle or Procedure	Membrane filter discs, 0.45 µm (Sartorius, Gelman, etc.).
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, 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 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.

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-$S0_4$ 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.

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 can not 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.

Sulphide/Sulfide, Total, Iodometric

Parameter	Sulfide, total (or Sulphide, total)
Analytical Method	Iodometric titration
EMS Code	**0125 X031**
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 sample is acidified and sparged with an inert gas. Hydrogen sulfide, thus liberated, is trapped in a zinc acetate solution. Excess iodine is added and back-titrated with standard sodium thiosulfate solution. Iodine consumed is equivalent to the trapped sulfide.
MDL	Typical: 0.5 mg/L Range: 0.5 to 16 mg S^{2-}/L
Matrix	Fresh water, industrial and domestic wastewater
Interferences and Precautions	Any reducing substance is liable to interfere; however, most are removed by the sparging technique.
Sample Handling and Preservation	Plastic or glass (500 mL), preserved immediately with 1 mL 2N zinc acetate/ 500mL sample.
Stability	M. H. T.: 7 days
Principle or Procedure	Acid dissociable sulfides are converted to H_2S and sparged into a trapping medium where they are determined iodometrically.
Precision	Authentic samples at concentrations of 3.58 and 4.87 mg S^{2-}/L gave respective coefficients of variation of 2.2 and 5.5%.
Accuracy	Relative error at a concentration of 5.21 mg/L was +6.5%.
Quality Control	The sodium thiosulfate should be standardized against commercially available potassium biniodate solution.

References

a) Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th edition, 1992. Method 4500-S^{2-}.

b) Methods for Chemical Analysis of Water and Waste EPA-600/4-79-020, USEPA, Revised March 1983. Method 376.1.

Revision History

February 14, 1994:	Publication in 1994 Laboratory Manual.
December 31, 2000:	SEAM codes replaced by EMS codes. Out of print reference deleted. 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	% Sensivitiy 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