

**3203**

**SITEWIDE CERCLA QUALITY ASSURANCE  
PROJECT PLAN VOLUME IV ATTACHMENT I  
FEMP LABORATORY ANALYTICAL METHODS  
MANUAL (CONTINUED) 4 MARCH 1992**

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**213  
ENCLOSURE**

VOLUME IV

3203

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**Fernald Environmental Management Project**

**SITEWIDE  
CERCLA QUALITY ASSURANCE  
PROJECT PLAN**

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**Attachment I  
FEMP Laboratory Analytical Methods Manual  
(continued)**

Prepared by

**Westinghouse Environmental Management Company of Ohio**

for the

**United States Department of Energy  
Fernald Office**

4 March 1992

3203

**VOLUME IV**  
**Methods for Conventional Parameters**

<b>Method</b>	<b>Method No.</b>
Cyanide (Total) Titrimetric	FM-CON-0010
Cyanide (Total) Spectrophotometric, Semiautomatic	FM-CON-0015
Soil pH	FM-CON-0020
Nitrogen, Nitrate/Nitrite (Colorimetric, Automated, Cadmium Reduction)	FM-CON-0030
Nitrogen, Nitrate/Nitrite (Spectrophotometric, Cadmium Reduction)	FM-CON-0040
Conductivity	FM-CON-0050
Total Kjeldahl Nitrogen	FM-CON-0060
Total Organic Carbon	FM-CON-0080
Alkalinity (Titrimetric)	FM-CON-0090
Alkalinity (Colorimetric)	FM-CON-0100
pH (Electrometric)	FM-CON-0110
Chloride (Colorimetric, Automated Ferricyanide)	FM-CON-0120
Sulfide	FM-CON-0130
Ammonia	FM-CON-0140
Hexavalent Chromium (Cr <sup>6+</sup> )	FM-CON-0150
Temperature	FM-CON-0160
Chloride (Titrimetric, Mercuric Nitrate)	FM-CON-0170
Oil and Grease (Infrared)	FM-CON-0175
Oil and Grease (Gravimetric Only)	FM-CON-0180
Percent Solids (Moisture)	FM-CON-0190
Total Petroleum Hydrocarbons Infrared	FM-CON-0200
Total Dissolved Solids	FM-CON-0210
Phosphorus Analysis Single Reagent Method	FM-CON-0220
Surfactants (MBAS)	FM-CON-0250
Phenolics, Total Recoverable (colorimetric, Automated 4-AAP with Distillation)	FM-CON-0260
Phenolics, Total Recoverable (Spectrophotometric Manual 4-AAP with Distillation)	FM-CON-0270
Sulfate (Colorimetric, Automated, Methylthymol Blue)	FM-CON-0280

VOLUME IV (cont.)

3203

**Method**

Sulfate (Turbidimetric)  
Fluoride  
Total Organic Halides  
Color  
Oxidation-Reduction Potential

**Method No.**

FM-CON-0290  
FM-CON-0300  
FM-CON-0320  
FM-CON-0330  
FM-CON-0340



3203

**Cyanide (Total)—Titrimetric**

**Working Linear Range:** Greater than 1.0 mg/L, infinite with dilution  
**Reporting Limit:** 1.0 mg/L  
**Reporting Units:** Water, mg/L; Solids, mg/kg  
**Matrix:** Water, wastes, soil, and sediment

**1.0 Scope and Application**

- 1.1 The method is applicable to the determination of cyanide in drinking, ground, surface, and saline waters; domestic and industrial aqueous wastes; soils; and sediments.
- 1.2 The titration procedure using silver nitrate with p-dimethylaminobenzyl-rhodanine indicator for measuring concentrations of cyanide exceeding 1 mg/L (0.25 mg/250 mL of absorbing liquid).

**2.0 Method Summary**

- 2.1 Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution (NaOH).
- 2.2 The titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

**3.0 Interferences**

- 3.1 Interferences are eliminated or reduced by using the distillation procedure described in the procedure.
- 3.2 The presence of surfactants may cause the sample to foam during refluxing. If foaming occurs, addition of an agent such as Dow Corning 544 antifoam (or equivalent) will prevent foam from collecting in the condenser.
- 3.3 High results may be obtained for samples that contain nitrate or nitrite. During distillation nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oxines. The compounds formed will

decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfuric acid.

- 3.4 Fatty acids will distill and form soaps under alkaline titration conditions, making the endpoint almost impossible to detect. If that occurs, the spectrophotometric method (FM-COM-0015) should be used.
- 3.5 If sulfides are present in the sample, they must be removed before preservation. Samples are preserved with 2 mL of 10 N sodium hydroxide (NaOH) per liter of sample (pH > 12) at the time of collection.

#### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling cyanide solutions and acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### 6.0 Apparatus

- 6.1 Reflux Distillation Apparatus: 1-liter boiling flask with inlet tube and provision for condenser. Gas absorber may be a Fisher-Milligan scrubber, or equivalent.
- 6.2 Buret: 5.0-mL Class A microburet, for titration.
- 6.3 Reflux Distillation Apparatus for Sulfide Removal: Sulfide scrubber may be a Wheaton Bubber No. 709682 with 29/42 joints, size 100 mL, or equivalent.

Air inlet should not be fritted. Cyanide absorption vessel should be the same as the sulfide scrubber, but the air inlet tube should be fritted.

6.4 Flowmeter: Lab Crest with stainless steel float, or equivalent.

#### 7.0 Routine Preventive Maintenance

7.1 No instrument is used for the method.

7.2 Examine glassware before each use for scratches and cracks, and replace as necessary.

#### 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

#### 8.2 Distillation and Preparation Reagents

8.2.1 Sodium Hydroxide Solution (NaOH), 1.25 N: Dissolve 50 grams of NaOH in water, and dilute to 1 liter with water.

8.2.2 Cadmium Carbonate ( $\text{CdCO}_3$ ): Powdered.

8.2.3 Ascorbic Acid: Crystals.

8.2.4 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ): Concentrated.

8.2.5 Magnesium Chloride Solution ( $\text{MgCl}_2$ ), 2.5 M: Dissolve 510 grams of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in water. Dilute with water to 1 liter.

8.2.6 Sodium Hydroxide Solution (NaOH), 10 N: Dissolve 400 grams NaOH in water. **Caution:** Add small amounts of NaOH at a time and allow to dissolve and cool before adding more. Cool, and dilute with water to 1 liter.

#### 8.3 Stock Standards and Titration Reagents

**Note:** Many standards and reagents can be obtained commercially.

- 8.3.1 Stock Cyanide Solution: Dissolve 2.51 grams of KCN and 1.6 grams NaOH (or 2 grams KOH) in 1 liter of water. Standardize with 0.0192 N silver nitrate ( $\text{AgNO}_3$ ).

**Note:** Solution should be standardized monthly because it gradually loses strength.

**Caution:** If KCN is acidified, cyanide gas will be released. Perform this procedure in a fume hood.

- 8.3.2 Standard (Intermediate) Cyanide Solution: Dilute 50.0 mL of stock (1 mg = 1 mL) to 1 liter with water.
- 8.3.3 Standard Cyanide Solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1 liter with water and store in glass stoppered bottle. 1 mL = 5.0  $\mu\text{g}$  CN (5.0 mg/L).
- 8.3.4 Standard Silver Nitrate Solution ( $\text{AgNO}_3$ ), 0.0192 N: Crush and dry at 40°C about 5 grams of  $\text{AgNO}_3$ . Dry to constant weight at 40°C. Dissolve 3.2647 grams dried  $\text{AgNO}_3$  in water. Dilute with water to 1 liter. Standardize against standard NaCl.
- 8.3.5 Rhodanine Indicator: Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 mL of acetone.
- 8.3.6 Sodium Hydroxide Solution (NaOH), 0.25 N: Dissolve 10 grams of NaOH in water, and dilute with water to 1 liter.
- 8.3.7 Standard Sodium Chloride Solution (NaCl), 0.0192 N: Dry 1.5 to 2 grams NaCl at 140°C. Dissolve 1.1222 grams dried NaCl in water. Dilute with water to 1 liter.
- 8.3.8 Potassium Chromate Indicator Solution: Dissolve 50 grams  $\text{K}_2\text{CrO}_4$  in a small amount of water. Add  $\text{AgNO}_3$  solution until a definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 liter with water.

## 9.0 Calibration Procedures

- 9.1 Standardization of Cyanide Standards: Since stock cyanide solution gradually loses strength, it should be standardized monthly to ensure that standard solutions made from it are accurate. The following procedure details the

standardization procedure and the calculations necessary to make standard CN solutions for the curve.

### 9.1.1 Standardize $\text{AgNO}_3$

9.1.1.1 Add 50 mL of water to titration casserole or beaker. Add 1.0 mL  $\text{K}_2\text{CrO}_4$  indicator, and titrate with  $\text{AgNO}_3$  until there is no more change in color. The endpoint is a pinkish-yellow color. This is a blank. Save titrated blank for color comparison.

9.1.1.2 Add 40 mL water to titration casserole or beaker. Carefully pipet 10.0 mL of 0.0192 N NaCl solution into the 40 mL of water. Add 1.0 mL  $\text{K}_2\text{CrO}_4$  indicator, and titrate with  $\text{AgNO}_3$  to same color intensity as blank.

9.1.1.3 Determine concentration of  $\text{AgNO}_3$  using the equation:

$$C_2 = \frac{(10 \text{ mL}) (0.0192)}{V_2} \quad (1)$$

Where:  $V_2$  is the volume of  $\text{AgNO}_3$

### 9.1.2 Standardize Cyanide Stock Solution

9.1.2.1 Add approximately 200 mL of water to 500-mL Erlenmeyer flask. Add 0.5 mL 1.25 N NaOH. Carefully pipet 20 mL CN stock solution into flask.

**Note:** NaOH must be put in flask before the CN standard.

9.1.2.2 Titrate flask contents with 0.0192 N  $\text{AgNO}_3$  using rhodanine indicator. The endpoint is sharp and indicated by a color change to salmon-pink. Titrate a blank of 250 mL of water and 0.5 mL 1.25 N NaOH.

9.1.2.3 Using equation (1), calculate concentration of CN stock solution:

$$C_2 = \frac{V_1 \times C_1}{20} \quad (2)$$

Where:

$V_1$  = volume of  $\text{AgNO}_3$  used in titration (mL  $\text{AgNO}_3$  for CN solution; mL  $\text{AgNO}_3$  for blank)

$C_1$  = concentration of  $\text{AgNO}_3$  determined in equation (1) (mg/L)

$V_2$  = volume of CN stock solution (20 mL)

$C_2$  = unknown concentration of CN solution (mg/L)

## 10.0 Sample Preparation

### 10.1 Distillation

10.1.1 Place 500 mL of sample, or an aliquot of sample diluted to 500 mL, in 1-liter boiling flask.

10.1.2 Add 50 mL of 1.25 N sodium hydroxide to absorbing tube, and dilute if necessary with water to obtain an adequate depth of liquid in absorber.

10.1.3 Connect boiling flask, condenser, absorber, and trap in the train. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust vacuum so that 1 bubble of air per second enters boiling flask through air inlet (thistle) tube.

**Note:** Bubble rate will not remain constant after reagents have been added and while heat is being applied to flask. It will be necessary to readjust air rate occasionally to prevent solution in boiling flask from backing up into air inlet tube.

10.1.4 Slowly add 25 mL of concentrated sulfuric acid through air inlet tube. Rinse tube with water, and allow airflow to mix flask contents for 3 minutes.

**Caution:** The fume hood must be on and the air stream flowing through the apparatus before sulfuric acid is added. The addition of sulfuric acid will begin the production of cyanide gas.

10.1.5 Add 20 mL of magnesium chloride solution through air inlet tube. Rinse tube with stream of water.

10.1.6 Heat solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Be sure to maintain the proper airflow through the system at all times so that all of the cyanide gas will be trapped in the sodium hydroxide solution.

10.1.7 Reflux for 1 hour.

10.1.8 Turn off heat and continue airflow for at least 15 minutes. After cooling boiling flask, disconnect absorber and close off vacuum source.

10.1.9 Drain solution from absorber into 250-mL volumetric flask. Rinse absorber tube with water, and collect washings in volumetric flask. Dilute to volume with water. This is the sample to be analyzed.

## 10.2 Preparation of Sediment or Soil Samples

10.2.1 Accurately weigh a representative 1- to 5-gram portion of wet sample, and transfer it to boiling flask. Add 500 mL of water. Shake or stir sample so that it is dispersed.

10.2.2 Distill sample using the same procedure outlined in Section 10.1, beginning with Step 10.1.2.

10.2.3 Using another sample aliquot, determine the percent solids of the sample with Method No. FM-CON-0190.

## 11.0 Sample Analysis

11.1 If sample contains more than 1 mg of CN, transfer distillate or a suitable aliquot diluted to 250 mL to a 500-mL Erlenmeyer flask. Add 10 to 12 drops of rhodanine indicator.

11.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink.

11.3 Titrate a water blank using the same amount of sodium hydroxide and rhodanine indicator as in the sample.

11.4 The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be conveniently used to obtain more precise titration. 10

**12.0 Calculations**

12.1 Calculate concentration of CN as follows:

$$\mu\text{g CN} = (a - b) \times \frac{N}{0.0192} \times 1000 \quad (3)$$

Where:

a = AgNO<sub>3</sub> titrated for sample (mL)  
b = AgNO<sub>3</sub> titrated for blank (mL)  
N = normality of AgNO<sub>3</sub>

12.2.2 For liquid samples, calculate the mg/L CN as follows:

$$\text{CN (mg/L)} = \frac{A}{B} \times \frac{C}{D} \quad (4)$$

Where:

A = CN from equation (3) above ( $\mu\text{g}$ )  
B = original sample (mL)  
C = distillate collected (mL)  
D = aliquot titrated (mL)

12.2.3 For solid samples, calculate mg/kg CN as follows:

$$\text{CN (mg/kg, dry wt.)} = \frac{A}{B} \times \frac{C}{D} \quad (5)$$

Where:

A = CN ( $\mu\text{g}$ )  
B = dry weight of original sample (grams)  
C = distillate collected (mL)  
D = aliquot titrated (mL)

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of analytical period
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA Contract Laboratory Program. *Statement of Work for Inorganics Analysis*. (SOW No. 788).
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Methods 335.2. March 1983.



3203

**Cyanide (Total)—Spectrophotometric, Semiautomatic**

**Working Linear Range:** 0.005 to 0.200 mg/L  
**Reporting Limit:** 0.005 mg/L  
**Reporting Units:** Water, mg/L; Solids, mg/kg  
**Matrix:** Water, wastes, soils, and sediments

**1.0 Scope and Application**

- 1.1 The method is applicable to the determination of cyanide in drinking, ground, surface, and saline waters; domestic and industrial aqueous wastes; soils; and sediments.
- 1.2 The working range of the semiautomated spectrophotometric method is 0.005 to 0.200 mg/L. Higher level samples must be diluted to fall within the working range.

**2.0 Method Summary**

- 2.1 Cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution (NaOH). The cyanide ion in the absorbing solution is then determined colorimetrically.
- 2.2 Cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridinebarbituric acid reagent. The absorbance is read at 578 nm for pyridine-barbituric acid.

**3.0 Interferences**

- 3.1 Interferences are eliminated or reduced by using the distillation procedure described in the procedure.
- 3.2 The presence of surfactants may cause the sample to foam during refluxing. If foaming occurs, addition of an agent such as Dow Corning 544 antifoam (or equivalent) will prevent foam from collecting in the condenser.

3.3 High results may be obtained for samples that contain nitrate or nitrite. During distillation nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oxines. The compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

3.4 If sulfides are present in the sample, they must be removed before preservation. Samples are preserved with 2 mL of 10 N sodium hydroxide (NaOH) per liter of sample (pH > 12) at the time of collection.

#### 4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling cyanide solutions and acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### 6.0 Apparatus

6.1 Reflux Distillation Apparatus: 1-liter boiling flask with inlet tube and provision for condenser. Gas absorber may be a Fisher-Milligan scrubber, or equivalent.

6.2 Buret: 5.0-mL Class A microburet, for titration.

6.3 Reflux Distillation Apparatus for Sulfide Removal: Sulfide scrubber may be a Wheaton Scrubber No. 709682 with 29/42 joints, size 100 mL, or equivalent.

3203

Air inlet should not be fritted. Cyanide absorption vessel should be the same as the sulfide scrubber, but the air inlet tube should be fritted.

6.4 Flowmeter: Lab Crest with stainless steel float, or equivalent.

6.5 Spectrophotometer suitable for measurements at 578 nm using 1.0-cm cell or larger.

### 7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the spectrophotometer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

### 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

#### 8.2 Distillation and Preparation Reagents

8.2.1 Sodium Hydroxide Solution (NaOH), 1.25 N: Dissolve 50 grams of NaOH in water, and dilute to 1 liter with water.

8.2.2 Cadmium Carbonate ( $\text{CdCO}_3$ ): Powdered.

8.2.3 Ascorbic Acid: Crystals.

8.2.4 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ): Concentrated.

8.2.5 Magnesium Chloride Solution ( $\text{MgCl}_2$ ), 2.5 M: Dissolve 510 grams of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in water. Dilute with water to 1 liter.

8.2.6 Sodium Hydroxide Solution (NaOH), 10 N: Dissolve 400 grams NaOH in water. **Caution:** Add small amounts of NaOH at a time and allow to

dissolve and cool before adding more. Cool, and dilute with water to 1 liter volumetric flask.

### 8.3 Stock Standards

**Note:** Many standards and reagents can be obtained commercially.

8.3.1 **Stock Cyanide Solution:** Dissolve 2.51 grams of KCN and 1.6 grams NaOH (or 2 grams KOH) in 1 liter of water. Standardize with 0.0192 N silver nitrate ( $\text{AgNO}_3$ ).

**Note:** Solution should be standardized monthly because it gradually loses strength.

**Caution:** If KCN is acidified, cyanide gas will be released. Perform this procedure in a fume hood.

8.3.2 **Standard Cyanide Solution:** Prepare by dilution from stock cyanide solution (see step 9.2.1 and Table 1).

8.3.3 **Standard Silver Nitrate Solution ( $\text{AgNO}_3$ ), 0.0192 N:** Crush and dry at  $40^\circ\text{C}$  about 5 grams of  $\text{AgNO}_3$ . Dry to constant weight at  $40^\circ\text{C}$ . Dissolve 3.2647 grams dried  $\text{AgNO}_3$  in water. Dilute with water to 1 liter.

8.3.4 **Rhodanine Indicator:** Dissolve 20 mg of p-dimethylaminobenzalrhodanine in 100 mL of acetone.

8.3.5 **Sodium Hydroxide Solution (NaOH), 0.25 N:** Dissolve 10 grams of NaOH in water, and dilute with water to 1 liter.

8.3.6 **Potassium Chromate Indicator Solution:** Dissolve 50 grams  $\text{K}_2\text{CrO}_4$  in a small amount of water. Add  $\text{AgNO}_3$  solution until a definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 liter with water.

### 8.4 Semiautomated Spectrophotometric Reagents

8.4.1 **Chloramine-T Solution, 0.4% w/v:** Dissolve 2.0 grams chloramine-T in 50 mL water (or 4.0 grams in 100 mL). Prepare fresh daily.

8.4.2 **Phosphate Buffer Solution No. 1, pH 5.2:** Dissolve 13.6 grams potassium dihydrogen phosphate and 0.28 gram disodium phosphate in 900 mL water, and dilute to 1 liter.

- 8.4.3 **Pyridine-Barbituric Acid Solution:** Transfer 15 grams of barbituric acid to 1-liter beaker. Wash sides of beaker with about 100 mL of water. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. **Caution:** Heat-liberating reaction. Dilute to about 900 mL with water and mix until all the acid has dissolved. Prepare in a fume hood. Transfer solution to 1-liter volumetric flask and dilute to mark. Store at  $4^{\circ} \pm 2^{\circ}\text{C}$ .
- 8.4.4 **Sampler Wash Solution (NaOH), 0.25 N:** Dissolve 10 grams NaOH in water, and dilute to 1 liter.

## 9.0 Calibration Procedures

- 9.1 **Standardization of Cyanide Standards:** Since stock cyanide solution gradually loses strength, it should be standardized monthly to ensure that standard solutions made from it are accurate. The following procedure details the standardization procedure and the calculations necessary to make standard CN solutions for the curve.

### 9.1.1 Standardize Cyanide Stock Solution

- 9.1.2.1 Add approximately 200 mL of water to 500-mL Erlenmeyer flask. Add 0.5 mL 1.25 N NaOH. Carefully pipet 20 mL CN stock solution into flask.

**Note:** NaOH must be put in flask before the CN standard.

- 9.1.2.2 Titrate flask contents with 0.0192 N  $\text{AgNO}_3$  using rhodanine indicator. The endpoint is sharp and indicated by a color change to salmon-pink. Titrate a blank of 250 mL of water and 0.5 mL 1.25 N NaOH.

- 9.1.2.3 Using equation (1), calculate concentration of CN stock solution.

$$C_2 = \frac{V_1 \times C_1}{20} \quad (1)$$

Where:

$V_1$  = volume of  $\text{AgNO}_3$  used in titration (mL  $\text{AgNO}_3$  for CN solution; mL  $\text{AgNO}_3$  for blank)

$C_1$  = concentration of  $\text{AgNO}_3$  determined in equation (1) (mg/L)

$V_2$  = volume of CN stock solution (20 mL)

$C_2$  = unknown concentration of CN solution (mg/L)

## 9.2 Preparation of Calibration Standards

9.2.1 Prepare a blank and at least three calibration standards (using the standardized calibration solutions) over the range of the analysis. One calibration standard must be at the CRDL. For a working range of 0 to 200  $\mu\text{g/L}$ , the following standards may be used:

Standard Solution diluted to 1 liter (mL)	Concentration $\mu\text{g CN/L}$
0	0
4.0	20
10.0	50
20.0	100
30.0	150
40.0	200

9.2.2 Add 10 grams of NaOH to each standard. Store at  $4^\circ \pm 2^\circ\text{C}$ .

## 10.0 Sample Preparation

### 10.1 Distillation

10.1.1 Place 500 mL of sample, or an aliquot of sample diluted to 500 mL, in 1-liter boiling flask.

10.1.2 Add 50 mL of 1.25 N sodium hydroxide to absorbing tube, and dilute if necessary with water to obtain an adequate depth of liquid in absorber.

10.1.3 Connect boiling flask, condenser, absorber, and trap in the train. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust vacuum so that 1 bubble of air per second enters boiling flask through air inlet (thistle) tube.

**Note:** Bubble rate will not remain constant after reagents have been added and while heat is being applied to flask. It will be necessary to readjust air rate occasionally to prevent solution in boiling flask from backing up into air inlet tube.

- 10.1.4 If samples contain  $\text{NO}_3$  and/or  $\text{NO}_2$ , add 2 grams of sulfamic acid after the air rate is set, through the air inlet tube. Mix for 3 minutes before adding the  $\text{H}_2\text{SO}_4$ .
- 10.1.5 Slowly add 25 mL of concentrated sulfuric acid through air inlet tube. Rinse tube with water, and allow airflow to mix flask contents for 3 minutes.
- Caution:** The fume hood must be on and the air stream flowing through the apparatus before the sulfuric acid is added. The addition of sulfuric acid will begin the production of cyanide gas.
- 10.1.6 Add 20 mL of magnesium chloride solution through air inlet tube. Rinse tube with stream of water.
- 10.1.7 Heat solution to boiling, taking care to prevent solution from backing up into and overflowing from air inlet tube. Be sure to maintain proper airflow through system at all times so that all cyanide gas is trapped in sodium hydroxide solution.
- 10.1.8 Reflux for 1 hour.
- 10.1.9 Turn off heat and continue airflow for at least 15 minutes. After cooling boiling flask, disconnect absorber and close off vacuum source.
- 10.1.10 Drain solution from absorber into 250-mL volumetric flask. Rinse absorber tube with water, and collect in volumetric flask. Dilute to volume with water. This is the sample to be analyzed.

## 10.2 Preparation of Sediment or Soil Samples

- 10.2.1 Accurately weigh a representative 1- to 5-gram portion of wet sample, and transfer it to boiling flask. Add 500 mL of water. Shake or stir sample so that it is dispersed.
- 10.2.2 Distill sample using the same procedure outlined in Section 10.1, beginning with Step 10.1.2.

- 10.2.3 Using another sample aliquot, determine the percent solids of the sample with Method No. FM-CON-0190.

## 11.0 Sample Analysis

- 11.1 Set up manifold. Pump reagents through system until steady baseline is obtained.
- 11.2 Prepare calibration standards. In addition, prepare a method blank consisting of water containing the same concentration of NaOH as the standards.
- 11.3 Fill sample cups and arrange on sampler wheel.
- 11.3.1 First, analyze the calibration standards, beginning with the highest concentration and proceeding to the lowest, ending with the blank.
- 11.3.2 Immediately after the calibration standards, analyze the initial calibration verification sample; then the method blank.
- 11.3.3 Finally, analyze the samples.
- 11.4 After every 20 samples, analyze the continuing calibration verification sample and the calibration blank.
- 11.5 End the analytical sequence by analyzing a continuing calibration verification sample and blank.

## 12.0 Calculations

- 12.1 Liquid Samples: Measure peak heights and prepare a standard calibration curve by plotting peak height as a function of concentration. To calculate the concentration of cyanide in the original sample:

$$\mu\text{g/L CN} = \frac{A \times 1,000}{B} \times \frac{50}{C} \quad (2)$$

3203

Where:

A = CN determined in the distillate per 250 mL ( $\mu\text{g/L}$ )  
 B = distillate used (mL)  
 C = original sample (mL)

12.2 Solid Samples: To calculate the concentration of cyanide in the original sample:

$$\text{CN, mg/kg} = \frac{A \times 0.25}{C \times (\% \text{ solids}/100)} \quad (3)$$

Where:

A = CN concentration determined from the standard calibration curve ( $\mu\text{g/L}$ )  
 C = wet weight of original sample (grams)  
 0.25 = conversion factor for distillate final volume

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

3203

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA Contract Laboratory Program. *Statement of Work for Inorganics Analysis*. (SOW No. 788).
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Methods 335.2, March 1983.

FERNALD/cn-spec.51



## Soil pH

<b>Working Linear Range:</b>	0 to 14
<b>Reporting Limit:</b>	N/A
<b>Reporting Units:</b>	pH units
<b>Matrix:</b>	Soil, sediment, or sludge
<b>Holding Time:</b>	Analyze immediately

### 1.0 Scope and Application

This is an electrometric procedure that can be applied to measuring pH in calcareous and noncalcareous soils.

### 2.0 Method Summary

The soil sample is mixed either with ASTM Type II water or with a calcium chloride ( $\text{CaCl}_2$ ) solution, depending whether the soil is considered to be calcareous or noncalcareous. The pH of the solution is then measured with a pH meter.

### 3.0 Interferences

- 3.1 Samples with very low or very high pH may give biased readings on the meter. For samples with true pH > 10, the measured pH may be biased low. This error can be minimized by using a low-sodium-error electrode. Strong acid solutions with true pH < 1 may yield pH measurements biased high.
- 3.2 Temperature fluctuations will cause measurement errors. The sample and the corresponding calibration standards should be at the same temperature.
- 3.3 Errors will occur when the electrodes become coated. If an electrode becomes coated with an oily material that cannot readily be rinsed off, the electrode can either (1) be cleaned with an ultrasonic bath or (2) be washed with detergent, rinsed several times with water, placed in a 1:10 HCl solution so that the lower third of the electrode is submerged, and then rinsed thoroughly with water.

#### **4.0 Safety Precautions**

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

- 6.1 pH Meter: The pH meter must be accurate and reproducible to 0.1 pH unit.
- 6.2 Reference and sensing Electrodes or a combination pH Electrode.
- 6.3 Magnetic Stirrer and Teflon-coated Stirring Bar.
- 6.4 Thermometer and pH Meter: Equipped with automatic temperature compensation and capable of measuring to  $\pm 0.1^\circ$ .
- 6.5 Beakers: Preferably borosilicate glass.
- 6.6 Analytical Balance: Capable of weighing  $\pm 0.01$  gram.

#### **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for pH meter and electrodes according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

- 8.1 Standard buffers are available commercially. Buffers must be about 3 pH units apart.
- 8.2 It is suggested that buffers of pH 4 and 7 or 7 and 10 be used for calibration.
- 8.3 Water: All references to water assume the use of ASTM Type II water.
- 8.4 Stock Calcium Chloride Solution ( $\text{CaCl}_2$ ), 3.6 M: Dissolve 1,059 grams of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in water in a 2-liter volumetric flask. Cool the solution, dilute it to volume with water, and mix well. To standardize solution, pipet 20 mL of stock calcium chloride solution into a 1-liter volumetric flask; dilute to mark with water; pipet 25 mL of working solution to a 100-mL beaker and add 1 mL of indicator, 5%  $\text{K}_2\text{CrO}_4$ ; titrate using commercially available 0.1 N  $\text{AgNO}_3$ ; calculate molarity of the stock calcium chloride solution using the equation  $M_1V_1 = M_2V_2$ .
- 8.5 Working Calcium Chloride Solution, 0.01 M: Dilute 50 mL of the stock 3.6 M  $\text{CaCl}_2$  to 18 liters with Type II water. Check the pH of the solution. If it is not between pH 5 and 6.5, adjust pH with  $\text{Ca}(\text{OH})_2$  or HCl. As a check on the preparation of this solution, the electrical conductivity of the working solution should be  $2.32 \pm 0.08$  mmhos/cm at 25°C.

## 9.0 Calibration Procedure

- 9.1 Because of the wide variety of pH meters and accessories, detailed operating procedures cannot be incorporated into this method. Calibrate pH meter using the manufacturer's directions.
- 9.2 Calibrate pH meter at a minimum of two points bracketing the expected pH of the samples and three pH units or more apart. A third buffer may be used as a QC check sample. The pH reading of the buffer should be within 0.05 pH unit of true pH.

## 10.0 Sample Preparation

- 10.1 Noncalcareous Soils

- 10.1.1 To 20 grams of soil in a 50-mL beaker, add 20 mL of Type II water and stir the suspension several times for 30 minutes.
- 10.1.2 Let the soil suspension stand for about 1 hour to allow any suspended clay to settle out from the suspension and to allow the sample to equilibrate to ambient temperature.
- 10.2 Calcareous Soils
- 10.2.1 To 10 grams of soil in a 50-mL beaker, add 20 mL of 0.01 M  $\text{CaCl}_2$  solution and stir the suspension several times for approximately 30 minutes.
- 10.2.2 Let the soil suspension stand for about 30 minutes to allow any suspended clay to settle out from the suspension and to allow the sample to equilibrate to ambient temperature.
- 11.0 Sample Analysis
- 11.1 Noncalcareous Soils
- 11.1.1 Adjust electrodes in clamps of electrode holder so that, upon lowering electrodes into beaker, the glass electrode shall be immersed just deep enough into the clear supernatant solution to establish good electrical contact through ground-glass joint or fiber-capillary hole. Insert electrodes into sample solution in this manner. For combination electrodes, immerse just below the suspension.
- 11.1.2 Record sample temperature.
- 11.1.3 If sample temperature differs by more than 2°C from buffer solution and if meter does not automatically adjust for temperature, correct measured pH values per manufacturer's directions.
- 11.1.4 Report results as "soil pH measured in water."
- 11.2 Calcareous Soils
- 11.2.1 Measure pH using step 11.1.1.
- 11.2.2 Record sample temperature.

11.2.3 If sample temperature differs by more than 2°C from buffer solution and if meter does not automatically adjust for temperature, correct measured pH values per manufacturer's directions.

11.2.4 Report results as "soil pH measured in 0.01 M CaCl<sub>2</sub>."

11.3 Rinse electrodes thoroughly between samples.

## 12.0 Data Treatment

Report pH results to nearest 0.1 pH unit. Report temperature results to nearest 1°C.

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

RPD            relative percent difference

## 15.0 References

U.S. EPA. *Test Methods for Evaluating Solid Waste*. SW846. Method 9045. September 1986.



## Nitrogen, Nitrate-Nitrite (Colorimetric, Automated, Cadmium Reduction)

**Working Linear Range:** 0.05 to 10.0 mg/L nitrate-nitrite as N  
**Reporting Limit:** 0.05 mg/L as N  
**Reporting Units:** mg/L as N  
**Matrix:** Water and wastes

### 1.0 Scope and Application

This method is applicable to the determination of nitrite only or of nitrite and nitrate combined, in fresh and saline waters and in domestic and industrial aqueous wastes. The applicable range of the method is 0.05 to 10.0 mg/L as N. The range may be extended with sample dilution.

### 2.0 Method Summary

A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically. Separate nitrate and nitrite values, rather than combined, are readily obtained by carrying out the procedure first with, then without, the copper-cadmium reduction step.

### 3.0 Interferences

- 3.1 Buildup of suspended matter in the reduction column will restrict sample flow. Since nitrate and nitrite are found in a soluble state, the sample may be prefiltered.
- 3.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.
- 3.3 Samples that contain large concentrations of oil or grease will coat the surface of the cadmium. This interference is eliminated by preextracting the samples with an organic solvent.

#### **4.0 Safety Precautions**

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

6.1 pH Meter.

6.2 Technicon Autoanalyzer, or equivalent.

6.2.1 Sampler.

6.2.2 Manifold or Analytical Cartridge.

6.2.3 Proportioning Pump.

6.2.4 Colorimeter equipped with a 15-mm or 50-mm tubular flow cell and 540-nm filters.

6.2.5 Recorder.

#### **7.0 Routine Preventive Maintenance**

7.1 Perform routine preventive maintenance for autoanalyzer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Nitrate- and Nitrite-free Water: Because of possible contamination, this should be prepared by passage through an ion exchange column comprising both strongly acidic-cation and strongly basic-anion exchange resins. The ion exchange column should be regenerated according to the manufacturer's instructions. Typically, ASTM Type II water is sufficient. All references to water assume the use of nitrate- and nitrite-free water.

8.2 Copper Sulfate Solution, 2%: Available commercially, or prepare by dissolving 20 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 mL of water and diluting to 1 liter.

8.3 Dilute Hydrochloric Acid, 6 N: Dilute 50 mL of concentrated HCl to 100 mL with water. **Caution:** Heat-liberating reaction.

8.4 Granulated Cadmium: 40-60 mesh, available commercially.

8.5 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate (step 8.2) in the following manner:

8.5.1 Wash cadmium with HCl (step 8.3) and rinse with water. The color of the cadmium should be silver; if it is not, wash cadmium again.

8.5.2 Swirl 10 grams cadmium in 100-mL portions of 2% solution of copper sulfate (step 8.2) for 5 minutes or until blue color partially fades, decant, and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

8.5.3 Wash cadmium-copper with water (at least 10 times) to remove all the precipitated copper. The color of the cadmium should be black; if not, wash cadmium again.

8.6 Preparation of Reduction Column (AAII): The reduction column is a U-shaped, 35-cm-long, 2-mm I.D. glass tube. Fill reduction column with

water to prevent entrapment of air bubbles during filling operations. Transfer copper-cadmium granules (step 8.5.3) to reduction column and place glass wool plug in each end. To prevent trapping air bubbles in reduction column, be sure that all pump tubes are filled with reagents before putting column into analytical system. Cadmium reduction columns prepared by the instrument manufacturer can be purchased.

**Note:** A 0.081-mm I.D. pump tube (purple) can be used in place of the 2-mm glass tube.

- 8.7 **Wash Solution:** Use water for unpreserved samples. For samples preserved with  $\text{H}_2\text{SO}_4$ , use 2 mL  $\text{H}_2\text{SO}_4$  per liter of wash water.
- 8.8 **Ammonium Chloride-EDTA Solution:** Dissolve 85 grams of reagent grade ammonium chloride and 0.1 gram of disodium ethylenediamine tetracetate in 900 mL of water. Adjust pH to 8.5 with concentrated ammonium hydroxide and dilute to 1 liter. Add 0.5 mL Brij-35 (available from instrument manufacturer) and mix well.
- 8.9 **Color Reagent:** To about 800 mL of water, add (while stirring) 100 mL concentrated phosphoric acid, 40 grams sulfanilamide, and 2 grams N-1-naphthylethylenediamine dihydrochloride. Stir until dissolved and dilute to 1 liter. Store in a brown bottle and keep in the dark when not in use. Solution is stable for several months if stored in the dark.
- 8.10 **Stock Nitrate Solution:** Dissolve 7.218 grams dried potassium nitrate ( $\text{KNO}_3$ ) in about 500 mL of water and dilute to 1 liter. Preserve with 2 mL of chloroform per liter. Solution is stable for 1 month. 1.0 mL = 1.0 mg  $\text{NO}_3\text{-N}$ .
- 8.11 **Stock Nitrite Solution:** Dissolve 6.072 grams potassium nitrite ( $\text{KNO}_2$ ) in about 500 mL of water and dilute to 1 liter. Preserve with 2 mL of chloroform and keep under refrigeration, protected from light. 1.0 mL = 1.0 mg  $\text{NO}_2\text{-N}$ .
- 8.12 **Standard Nitrate Solution:** Dilute 10.0 mL of stock nitrate solution (step 8.10) to 1 liter. 1.0 mL = 0.01 mg  $\text{NO}_3\text{-N}$ . Preserve with 2 mL of chloroform per liter. Solution is stable at least for 6 months.
- 8.13 **Standard Nitrite Solution:** Dilute 10.0 mL of stock nitrite (step 8.11) solution to 1,000 mL. 1.0 mL = 0.01 mg  $\text{NO}_2\text{-N}$ . Solution is unstable; prepare fresh before use.

- 8.14 Using standard nitrate solution (step 8.12), prepare the following standards in 100-mL volumetric flasks. As least one nitrite standard should be compared to a nitrate standard at the same concentration to verify the efficiency of the reduction column.

Concentration, mg NO <sub>2</sub> -N or NO <sub>3</sub> -N/L	mL Standard Solution/100 mL
0.0	0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0
2.00	20.0
4.00	40.0
6.00	60.0

**Note:** When the samples to be analyzed are saline waters, substitute ocean water should be used for preparing the standards; otherwise water is used. The composition of substitute ocean water is:

NaCl	24.53 g/L	MgCl <sub>2</sub>	5.20 g/L	Na <sub>2</sub> SO <sub>4</sub>	4.09 g/L
CaCl <sub>2</sub>	1.16 g/L	KCl	0.70 g/L	NaHCO <sub>3</sub>	0.20 g/L
KBr	0.10 g/L	H <sub>3</sub> BO <sub>3</sub>	0.03 g/L	SrCl <sub>2</sub>	0.03 g/L
NaF	0.003 g/L				

- 8.15 Sodium Hydroxide (NaOH), 1 N: Dissolve 40 grams NaOH in about 800 mL water. Care should be taken as the solution will become hot. Add NaOH pellets a few at a time. Dilute to 1 liter.
- 8.16 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>), 1 N: Add 28 mL concentrated H<sub>2</sub>SO<sub>4</sub> slowly and carefully to about 900 mL water. **Caution:** Heat-liberating reaction. Dilute to 1 liter.

## 9.0 Calibration Procedures

- 9.1 Prepare at least four standards covering the working linear range of the samples (see step 8.14). Also prepare a calibration blank (nitrate- and nitrite-free water).

- 9.2 Analyze the standard solutions and the method blank. Prepare a standard curve by plotting peak height as a function of concentration.
- 9.3 Immediately after the curve is prepared, analyze a calibration verification sample that is different from the calibration solution. If the result is within the control chart limit, then sample analysis may proceed. If not, recalibrate the instrument.

#### 10.0 Sample Preparation

- 10.1 Allow samples to come to room temperature.
- 10.2 If sample pH is below 5 or above 9, adjust pH to between 5 and 9 with either 1 N NaOH (step 8.15) or 1 N H<sub>2</sub>SO<sub>4</sub> (step 8.16).

#### 11.0 Sample Analysis

- 11.1 Set up manifold according to manufacturer's directions.
- 11.2 Allow both colorimeter and recorder to warm up about 30 minutes. Obtain a stable baseline with all reagents, feeding water through the sample line.

**Note:** Condition column by running a 1-mg/L standard for 10 minutes if a new reduction column is being used.

- 11.3 Place appropriate nitrate and nitrite standards in sampler in order of decreasing concentration of nitrogen. Before unknown samples are analyzed, a laboratory control sample and method blank should be analyzed.
- 11.4 Switch sample line to sampler and start analysis.

#### 12.0 Calculations

As needed, prepare separate curves for nitrate and total nitrite/nitrate. Compute concentration of samples by comparing sample peak heights with standard curve.

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/10	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

### 15.0 References

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 353.2. March 1983.
- 15.2 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Method 418F. 1985.



## Nitrogen, Nitrate-Nitrite (Spectrophotometric, Cadmium Reduction)

<b>Working Linear Range:</b>	0.01 to 1.0 mg/L nitrate-nitrite as N
<b>Reporting Limits:</b>	0.01 mg/L as N
<b>Reporting Units:</b>	mg/L as N
<b>Matrix:</b>	Water and wastes

### 1.0 Scope and Application

The method is applicable to the determination of nitrite only or nitrite and nitrate combined in drinking, surface, and saline waters and domestic and industrial aqueous wastes. The applicable range of the method is 0.01 to 1.0 mg/L as N. The range may be extended with sample dilution.

### 2.0 Summary of Method

A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured spectrophotometrically. Separate rather than combined nitrate-nitrite values are readily obtained by carrying out the procedure first with, then without, the copper-cadmium reduction step.

### 3.0 Interferences

- 3.1 Buildup of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be prefiltered through a glass fiber filter or a 0.45-micron membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove most of the particulate matter present in the sample.
- 3.2 Low results might be obtained for samples that contain high concentrations of iron, copper, or other metals. EDTA is added to the samples to eliminate such interference. Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. Interference is eliminated by preextracting the sample with an organic solvent.

3203

- 3.3 The procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. Nitrite may be determined by the procedure without the reduction step.

#### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling acids and bases must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### 5.0 Sample Collection and Handling

- 5.1 Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

**Caution:** Do not preserve samples for reduction column using mercuric chloride.

#### 6.0 Apparatus

- 6.1 Reduction Column: Available commercially, or constructed from a 100-mL pipet by removing the top portion. The column may also be constructed from two pieces of tubing joined end to end. A 10-mm I.D. length of 3-cm I.D. tubing is joined to a 25-cm length of 3.5-mm I.D. tubing.
- 6.2 Spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer.

**7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the spectrophotometer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Standards**

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Dilute Hydrochloric Acid, 6 N: Dilute 50 mL of concentrated HCl to 100 mL with water. **Caution:** Heat-liberating reaction.
- 8.3 Copper Sulfate Solution, 2%: Dissolve 20 grams of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 500 mL of water and dilute to 1 liter.
- 8.4 Ammonium Chloride-EDTA Solution: Dissolve 13 grams of ammonium chloride and 1.7 grams disodium ethylenediamine tetracetate in 900 mL of water. Adjust pH to 8.5 with concentrated ammonium hydroxide and dilute to 1 liter.
- 8.5 Dilute Ammonium Chloride-EDTA Solution: Dilute 300 mL of ammonium chloride-EDTA solution (step 8.4) to 500 mL with water.
- 8.6 Granulated Cadmium, 40-60 Mesh: Available commercially from E M Laboratories, Inc., 500 Executive Boulevard, Elmsford, NY 10523, Cat. 2001 Cadmium, Coarse Powder; or equivalent.
- 8.7 Copper-Cadmium: Cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner:
- 8.7.1 Wash cadmium with dilute HCl (step 8.2) and rinse with water. The color of the cadmium should be silver; if it is not, wash cadmium again.

- 8.7.2 Swirl 25 grams cadmium in 100-mL portions of a 2% solution of copper sulfate (step 8.3) for 5 minutes or until blue color partially fades, decant, and repeat with fresh copper sulfate until a brown colloidal precipitate forms.
- 8.7.3 Wash copper-cadmium with water (at least 10 times) to remove all the precipitated copper. The color of the cadmium should be black; if it is not, wash cadmium again.
- 8.8 Preparation of Reaction Column: Insert glass wool plug into bottom of reduction column and fill with water. Add sufficient copper-cadmium granules to produce a column 18.5 cm long. Maintain a level of water above the copper-cadmium granules to avoid trapping air. Wash column with 200 mL of dilute ammonium chloride solution (step 8.5). Activate column by passing through the column 100 mL of a solution composed of 25 mL of a 1.0-mg/L  $\text{NO}_3\text{-N}$  standard and 75 mL of ammonium chloride-EDTA solution (step 8.4). Use a flow rate between 7 and 10 mL per minute.
- 8.9 Color Reagent
- 8.9.1 Dissolve 10 grams sulfanilamide and 1 gram N-(1-naphthyl)-ethylenediamine dihydrochloride in a mixture of 100 mL concentrated phosphoric acid and 800 mL of water and dilute to 1 liter with water. **Caution:** Heat-liberating reaction.
- 8.9.2 Store under refrigeration, protected from light. Solution is stable for at least 1 month.
- 8.10 Zinc Sulfate Solution: Dissolve 100 grams  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in water and dilute to 1 liter with nitrate- and nitrite-free water.
- 8.11 Sodium Hydroxide Solution, 6 N: Dissolve 240 grams NaOH in 500 mL water, cool, and dilute to 1 liter.
- 8.12 Stock Nitrate Solution: Dissolve 7.218 grams  $\text{KNO}_3$  that has been dried in an oven at  $105^\circ\text{C}$  for 24 hours and cooled in a desiccator in water and dilute to 1 liter. Preserve with 2 mL of chloroform per liter. This solution is stable for at least 6 months. 1.0 mL = 1.00 mg  $\text{NO}_3\text{-N}$ .
- 8.13 Standard Nitrate Solution: Dilute 10.0 mL of nitrate stock solution (step 8.12) to 1 liter with water. 1.0 mL = 0.01 mg  $\text{NO}_3\text{-N}$ .

- 8.14 **Stock Nitrite Solution:** Use a fresh bottle of  $\text{KNO}_2$ . Dry 7 grams in a tared 125-mL beaker for about 24 hours to a constant weight in a desiccator containing concentrated  $\text{H}_2\text{SO}_4$ . Adjust weight of dry  $\text{KNO}_2$  to 6.072 grams. Dissolve in 50 mL water and transfer to 1-liter volumetric flask. Dilute to mark and preserve with 2 mL chloroform. Store in a sterilized bottle under refrigeration, protected from light. This solution is stable for at least 1 month. ( $\text{KNO}_2$  is easily reduced.) 1.0 mL = 1.00 mg  $\text{NO}_2\text{-N}$ .
- 8.15 **Standard Nitrite Solution:** Dilute 10.0 mL of stock nitrite solution (step 8.14) to 1 liter with water. 1.0 mL = 0.01 mg  $\text{NO}_2\text{-N}$ . This solution is unstable; prepare fresh before each use.
- 8.16 Using standard nitrate solution (step 8.13) prepare the following standards in 100-mL volumetric flasks:

Concentration, mg $\text{NO}_3\text{-N/L}$	mL of Standard Solution/100.0 mL
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

- 8.17 **Concentrated Ammonium Hydroxide.**

## 9.0 Calibration Procedures

- 9.1 Prepare at least four standards covering the working linear range of the samples (see step 8.16) and one method blank (ASTM Type II water). At least one  $\text{NO}_2$  standard should be compared to a reduced nitrate standard at the same concentration to verify efficiency of the reduction column.
- 9.2 Analyze the standard solution and the method blank using the procedure presented in steps 11.1 to 11.4. Prepare a standard curve by plotting absorbance as a function of concentration.
- 9.3 Also prepare and analyze one mid-range nitrite standard as a continuing calibration verification sample (CCVS) to verify the efficiency of the reduction column. If the result is within control chart limits, then sample

analysis may proceed. If not, recalibrate the instrument. The verification solution must be from a source different from the calibration solution.

9.4 A CCVS should be analyzed after every 10 samples.

#### 10.0 Sample Preparation

10.1 Turbidity Removal: One of the following methods may be used to remove suspended matter.

10.1.1 Filter sample through a glass fiber filter or a 0.45-micron membrane filter.

10.1.2 Add 1 mL zinc sulfate solution (step 8.10) to 100 mL of sample and mix thoroughly. Add 0.4 to 0.5 mL sodium hydroxide solution (step 8.11) until pH is 10.5 as determined with a pH meter. Let treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45-micron membrane filter.

10.2 Oil and Grease Removal: Adjust the pH of 100 mL of filtered sample to 2 by addition of concentrated HCl. Extract oil and grease from aqueous solution with two 25-mL portions of a nonpolar solvent (Freon, chloroform, or equivalent).

10.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either concentrated HCl or concentrated  $\text{NH}_4\text{OH}$ . This is done to obtain a sample pH of 8.5 (step 11.1).

#### 11.0 Sample Analysis

11.1 Add 75 mL of ammonium chloride-EDTA solution (step 8.4) to 25.0 mL of sample or an aliquot diluted to 25.0 mL and mix.

11.2 Pour sample into column and collect sample at a rate of about 7 to 10 mL per minute.

11.3 Discard the first 25 mL of sample, and collect the rest (about 70 mL) in original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent (see step 11.5).

- 11.4 Prepare columns for storage. Pass 50 mL of  $\text{NH}_4\text{CL-EDTA}$  solution through the system. Store column in fresh portion of the solution, never letting it become dry.

**Note:** If sample concentration exceeds 1.0 mg  $\text{NO}_3\text{-N/L}$ , sample may require dilution before analysis.

- 11.5 Add 2.0 mL of color reagent to 50.0 mL of sample. Allow about 10 minutes for color development. Measure the absorbance at 540 nm against a reagent blank within 2 hours of reducing the sample.
- 11.6 Analyze standards exactly as the sample.

## 12.0 Calculations

- 12.1 Obtain a standard curve by plotting the adsorbance of standards run by the above procedure against  $\text{NO}_3\text{-N}$  mg/L. Compute concentration of samples by comparing sample absorbance with standard curve.
- 12.2 If less than 25 mL of sample is used for analysis, the following equation should be used:

$$\text{mg/L NO}_2 + \text{NO}_3 \text{ as N} = \frac{A \times 25}{\text{mL sample used}} \quad (1)$$

Where:

A = concentration (mg/L as N) of nitrate from standard curve

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

3203

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corr. Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/10	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

## 15.0 References

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 353.3. March 1983.
- 15.2 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed. Method 418C. 1985.

FERNALD/n-spec.51



3203

## Conductivity

**Working Linear Range:** NA  
**Reporting Limit:**  $\mu\text{mhos/cm}$   
**Reporting Units:**  $\mu\text{mhos/cm}$   
**Matrix:** Water

### 1.0 Scope and Application

This method is applicable to drinking, ground, surface, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

- 2.1 Sample conductivity is measured using a self-contained conductivity meter (Wheatstone bridge-type, or equivalent).
- 2.2 Ideally, samples are analyzed at 25°C. If not, temperature corrections are made and results reported at 25°C.

### 3.0 Interferences

- 3.1 Platinum electrodes can degrade and cause erratic results. If this occurs, as evidenced by erratic results or flaking off of the platinum black, the electrode should be replatinized according to the manufacturer's directions.
- 3.2 The conductance cell can become coated with oil and other materials. It is essential that the cell be thoroughly rinsed and, if necessary, cleaned between samples.
- 3.3 Temperature variations and connections can represent the larger sources of potential error.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples

determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Conductivity Meter and Cell: Choose an instrument capable of measuring conductivity with an error not exceeding 1% or 1  $\mu\text{mho/cm}$ , whichever is greater.
- 6.2 Conductivity Cell: Platinum electrode or nonplatinum electrode.
- 6.3 Thermometer: Capable of being read to the nearest 0.1°C and covering the range 23° to 27°C.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the conductivity meter according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

- 8.1 Conductivity Water: Deionized water with a conductivity < 1  $\mu\text{mho/cm}$ .
- 8.2 Standard Potassium Chloride (KCl), 0.0100 M: Dissolve 0.7456 gram anhydrous KCl in conductivity water. Dilute to 1,000 mL. Store in a glass-stoppered borosilicate glass bottle.

- 8.2.1 The conductivity of this standard solution at 25°C is 1,413  $\mu\text{mhos/cm}$ .
- 8.2.2 Weaker or stronger standard conducting solution can be prepared following Table 1:

**Table 1. KCl Standard Conductivity**

grams KCl/L	Concentration M	Conductivity ( $\mu\text{mhos/cm}$ )
0.075	0.001	147.0
3.728	0.05	6668
14.912	0.2	24,820

## 9.0 Calibration Procedure

- 9.1 Instrument shall be standardized with KCl solution daily before use according to the manufacturer's directions.
- 9.2 Determine cell constant. Rinse conductivity cell with at least three portions of 0.01 M KCl solution (1,413  $\mu\text{mhos/cm}$ ). Measure resistance of a fourth portion and note temperature. Temperature of KCl should first be adjusted to  $25.0^\circ \pm 0.1^\circ\text{C}$ . Compute cell constant, C:

$$C = (0.001413) (R_{\text{KCl}}) [1 + 0.0191(t - 25)] \quad (1)$$

Where:

$$\begin{aligned} R_{\text{KCl}} &= \text{measured resistance (ohms)} \\ t &= \text{observed temperature (nearest } 0.1^\circ\text{C)} \end{aligned}$$

## 10.0 Sample Preparation

Allow sample to come to room temperature, as close to 25°C as possible. Filter the sample if the conductivity is not measured within 24 hours of sample collection.

3203

**11.0 Sample Analysis**

- 11.1 Rinse cell with one or more portions of sample.
- 11.2 Measure sample resistance or conductivity and record temperature.
- 11.3 Calculate conductivity at 25°C by either formula 2 or 3, whichever is applicable.

**12.0 Calculations**

- 12.1 When sample resistance is measured, conductivity at 25°C is:

$$K = \frac{1,000,000 \times C}{R_m [1 + 0.0191 (t - 25)]} \quad (2)$$

Where:

K	=	conductivity ( $\mu\text{mhos/cm}$ )
C	=	cell constant ( $\text{cm}^{-1}$ )
$R_m$	=	measured resistance of sample (ohms)
t	=	temperature of measurement (nearest 0.1°C)

- 12.2 When sample conductivity is measured, conductivity at 25°C is:

$$K = \frac{K_m C}{[1 + 0.0191 (t - 25)]} \quad (3)$$

Where:

K	=	conductivity ( $\mu\text{mhos/cm}$ )
$K_m$	=	measured conductivity ( $\mu\text{mhos/cm}$ at t°C)
C	=	cell constant ( $\text{cm}^{-1}$ )
t	=	temperatures of measurement (nearest 0.1°C)

- 12.3 If sample temperature is below 25°C, add 2% of the reading per degree.

12.4 If sample temperature is above 25°C, subtract 2% of the reading per degree.

### 13.0 Data Package Deliverables

Data package deliverables are determined by Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

### 15.0 References

- 15.1 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Method 403. 1985.
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 120. March 1983.

3203

15.3 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed. SW 846, with Final Update I, Method 9050. November 1986.

FERNALD/conduct.51

FM-CON-0060

## Total Kjeldahl Nitrogen

**Working Linear Range:** 0.1 to 100 mg/L (matrix-dependent)  
**Reporting Limit:** 0.1 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and wastes

### 1.0 Scope and Application

- 1.1 The method covers the determination of total Kjeldahl nitrogen (TKN) in drinking, surface, and saline waters and domestic and industrial aqueous wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones, and some refractory tertiary amines.
- 1.2 Two alternatives are listed for the determination of ammonia after distillation: the titrimetric method, which is applicable to concentrations above 1 mg N/liter; or the Nesslerization method, which is applicable to concentrations below 1 mg N/liter.
- 1.3 The method is described for macro and micro glassware systems.

### 2.0 Method Summary

The sample is heated in the presence of concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{HgSO}_4$  and evaporated until  $\text{SO}_3$  fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, treated, and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization or titration.

### 3.0 Interferences

High nitrate concentrations ( $10\times$  the TKN level or more) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

#### **4.0 Safety Precautions**

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

- 6.1 Digestion Apparatus: A Kjeldahl digestion apparatus with 100- or 800-mL flasks and suction takeoff to remove SO<sub>3</sub> fumes and water.
- 6.2 Distillation Apparatus: The macro Kjeldahl flask is connected to a condenser and an adapter so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.
- 6.3 Spectrophotometer: Double beam, for use at 400 to 425 nm with a light path of 1 cm or longer.

#### **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the spectrophotometer is performed according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Mercuric Sulfate Solution: Dissolve 8 grams red mercuric oxide (HgO) in 50 mL of 1:4 sulfuric acid (10.0 mL concentrated H<sub>2</sub>SO<sub>4</sub> : 40 mL water) and dilute to 100 mL with water. **Caution:** Heat-liberating reaction.

8.3 Sulfuric Acid-Mercuric Sulfate-Potassium Sulfate Solution: Dissolve 267 grams K<sub>2</sub>SO<sub>4</sub> in 1,300 mL water and 400 mL concentrated H<sub>2</sub>SO<sub>4</sub>. Add 50 mL mercuric sulfate solution and dilute to 2 liters with water.

8.4 Sodium Hydroxide-Sodium Thiosulfate Solution: Dissolve 500 grams NaOH and 25 grams Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> · 5H<sub>2</sub>O in water and dilute to 1 liter.

8.5 Mixed Indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with 1 volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

8.6 Boric Acid Solution: Dissolve 20 grams boric acid, H<sub>3</sub>BO<sub>3</sub>, in water and dilute to 1 liter with water.

8.7 Sulfuric Acid, Standard Solution, (0.02 N): Prepare a stock solution of approximately 0.1 N acid by diluting 3 mL of concentrated H<sub>2</sub>SO<sub>4</sub> (specific gravity 1.84) to 1 liter with water. Dilute 200 mL of this solution to 1 liter with water. **Caution:** Heat-liberating reaction.

8.7.1 Sodium Carbonate Solution (Na<sub>2</sub>CO<sub>3</sub>), 0.05 N: Dry 3 to 5 grams primary standard Na<sub>2</sub>CO<sub>3</sub> at 250°C for 4 hours and cool in a desiccator.

8.7.2 Weigh 2.5 ± 0.200 grams, and transfer to a 1-liter volumetric flask.

8.7.3 Fill flask to mark with water, and dissolve and mix reagent. Do not keep longer than 1 week.

8.8 Stock Ammonium Chloride Solution, 1.0 mL = 1.0 mg NH<sub>3</sub>-N: Dissolve 3.819 grams NH<sub>4</sub>Cl in water and dilute to 1 liter.

- 8.8.1 Standardize the 0.02 N  $\text{H}_2\text{SO}_4$  against 15 mL 0.05 N  $\text{Na}_2\text{CO}_3$  solution with about 60 mL water in a beaker by titrating potentiometrically to pH of about 5.
- 8.8.2 Lift out electrodes, rinse into the same beaker, and boil gently for 3 to 5 minutes under a watch glass cover.
- 8.8.3 Cool to room temperature, rinse cover glass into beaker, and finish titrating to the pH inflection point.
- 8.8.4 Normality, N = 
$$\frac{A \times B}{53.00 \times C}$$

Where:

A	=	mass of $\text{Na}_2\text{CO}_3$ weight into 1-liter flask (grams)
B	=	volume of $\text{Na}_2\text{CO}_3$ solution taken for titration (mL)
C	=	volume of acid used (mL)

- 8.9 Standard Ammonium Chloride Solution, 1.0 mL = 0.01 mg  $\text{NH}_3\text{-N}$ : Pipet 10.0 mL of stock ammonium chloride solution into 1-liter volumetric flask. Dilute to mark and mix.
- 8.10 Nessler Reagent: Dissolve 100 grams of mercuric iodide and 70 grams potassium iodide in a small volume of water. Add this mixture slowly while stirring to a cooled solution of 160 grams of NaOH in 500 mL of water. Dilute the mixture to 1 liter. The solution is stable for at least 1 year if stored in a pyrex bottle protected from light.
- 9.0 Calibration Procedures**
- 9.1 Colorimetric Determination: Prepare a series of Nessler tube standards. It is not necessary to prepare all the standards; four standards bracketing expected concentration range and one blank are acceptable.

3203

mL of Standard 1.0 mL = 0.01 mg NH <sub>3</sub> -N	mg NH <sub>3</sub> -N/50.0 mL
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

- 9.2 Dilute each tube to 50 mL with water, and then add 1 mL of Nessler Reagent and mix. After approximately 20 minutes, measure the absorbance at 425 nm against the blank. Prepare a calibration curve by plotting absorbance as a function of concentration. Repeat the process with the samples first adding 1 mL of Nessler reagent to 50 mL of sample, then measuring the absorbance of the solution after about 20 minutes. The concentration of the sample can be extrapolated from the standard curve.

#### 10.0 Sample Preparation

Sample preparation is not necessary.

#### 11.0 Sample Analysis

- 11.1 The distillation apparatus should be presteamed before use by distilling a 1:1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).
- 11.2 Macro Kjeldahl System
- 11.2.1 Transfer an aliquot of sample into an 800-mL Kjeldahl flask. Sample size can be determined as follows:

Expected Kjeldahl Nitrogen in Sample (mg/L)	Sample Size (mL)
0-5	500
5-10	250
10-20	100
20-50	50.0
50-500	25.0

11.2.2 If required, dilute the sample to 500 mL with water and add 100 mL sulfuric acid-mercuric sulfate-potassium sulfate solution to the sample. Evaporate the mixture in the Kjeldahl apparatus until SO<sub>3</sub> fumes are given off and the solution turns colorless or pale yellow. Continue heating for an additional 30 minutes. Cool residue and add 300 mL water.

11.2.3 Adjust pH of digestate by carefully adding 100 mL of sodium hydroxide-thiosulfate solution without mixing.

**Note:** Slow addition of heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free ammonia. Do not mix until digestion flask has been connected to distillation apparatus.

11.2.4 Place 50 mL of 2% boric acid solution into distillate receiving flask.

11.2.5 Connect Kjeldahl flask to condenser so that tip of condenser or extension of condenser tip is below level of boric acid solution in receiving flask.

11.2.6 Distill 300 mL at the rate of 6 to 10 mL/min.

11.2.7 Dilute distillate to 500 mL in flask. Flasks should be marked at the 350- and 500-mL volumes. With such marking it is not necessary to transfer distillate to volumetric flasks. For concentrations above 1 mg/L, ammonia can be determined titrimetrically; for concentrations below that value, it should be determined colorimetrically.

11.3 Micro Kjeldahl System

11.3.1 Place 50.0 mL of sample (or an aliquot diluted to 50 mL) in a 100-mL Kjeldahl flask and add 10 mL sulfuric acid-mercuric sulfate-potassium sulfate solution. Evaporate mixture in Kjeldahl apparatus until SO<sub>3</sub> fumes are given off.

off and solution turns colorless or pale yellow; then digest for 30 minutes more. Cool residue and add 30 mL water.

- 11.3.2 Adjust pH of digestate by carefully adding 10 mL of sodium hydroxide-thiosulfate solution without mixing. Do not mix until digestion flask has been connected to distillation apparatus.
- 11.3.3 Transfer 5 mL of 2% boric acid solution into distillate receiving flask.
- 11.3.4 Connect Kjeldahl flask to condenser so that tip of condenser or extension of the condenser tip is below level of boric acid solution in receiving flask or 50-mL short-form Nessler tube.
- 11.3.5 Steam distill 30 mL at the rate of 6 to 10 mL/min.
- 11.3.6 Dilute distillate to 50 mL. For concentrations above 1 mg/L, ammonia can be determined titrimetrically; for concentrations below that value, it should be determined colorimetrically.
- 11.4 Determination of Ammonia in Distillate
- 11.4.1 Titrimetric Determination: Add 3 drops of mixed indicator to distillate and titrate ammonia with 0.02 N  $H_2SO_4$ , matching the endpoint against a blank containing the same volume of distilled water and  $H_3BO_3$  solution.
- 11.4.2 Colorimetric Determination: Add 1 mL of Nessler Reagent to 50 mL of sample, then measure the absorbance of the solution after about 20 minutes. The concentration of the sample can be extrapolated from the standard curve.
- 12.0 Calculations
- 12.1 If titrimetric procedure is used, calculate TKN in original sample as follows:

$$\text{TKN, mg/L} = \frac{(A - B) N \times F \times 1000}{S}$$

3203

Where:

A = volume of standard 0.020 N H<sub>2</sub>SO<sub>4</sub> solution used in titrating sample (mL)

B = volume standard 0.020 N H<sub>2</sub>SO<sub>4</sub> solution used in titrating blank (mL)

N = normality of sulfuric acid solution

F = weight of nitrogen at 14 mg

S = volume of sample digested (mL)

If sulfuric acid is exactly 0.02 N, the formula is shortened to:

$$\text{TKN, mg/L} = \frac{(A - B) \times 280}{S}$$

12.2 If Nessler procedure is used, calculate TKN in the original sample as:

$$\text{TKN, mg/L} = \frac{A \times 1000 \times B}{C \times D}$$

Where:

A = mass of NH<sub>3</sub>-N read from curve (mg)

B = volume of total distillate collected, including the H<sub>3</sub>BO<sub>3</sub> (mL)

C = volume of distillate taken for Nesslerization (mL)

D = volume of original sample taken (mL)

12.3 Calculate organic Kjeldahl nitrogen as:

$$\text{Organic Kjeldahl Nitrogen} = \text{TKN} - (\text{NH}_3\text{-N})$$

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

### 15.0 References

- 15.1 *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Methods 420A and 420B. 1985.
- 15.2 *Methods for Chemical Analysis of Water and Wastes*. PB84. Method 351.3. March 1983.

FM-CON-0080

## Total Organic Carbon

**Working Linear Range:** Instrument-dependent  
**Reporting Limits:** 1 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and wastes

### 1.0 Scope and Application

The method is applicable to the measurement of organic carbon in drinking, ground, surface, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

- 2.1 Total carbon is defined as all the carbon present in a sample and comprises total organic and inorganic carbon. Each carbon analyzer is different, and each instrument handles total inorganic carbon differently.
- 2.1.1 Total Inorganic Carbon (TIC): Refers to carbon that is converted to carbon dioxide after acidification of a sample. TIC includes all dissolved carbon dioxide, bicarbonate, and carbonate species and is reported in terms of total mass of carbon per unit of sample (e.g., mg C/L).
- 2.1.2 Total Organic Carbon (TOC): Refers to all carbon atoms bonded in organic molecules that are converted to carbon dioxide by oxidation after inorganic carbon has been removed or subtracted.
- 2.2 Organic carbon is measured using a carbonaceous analyzer. Organic carbon in a sample is converted to carbon dioxide (CO<sub>2</sub>) by either catalytic combustion or wet chemical oxidation, depending on the analytical instrument chosen. The CO<sub>2</sub> formed is then either measured directly by an infrared detector or converted to methane (CH<sub>4</sub>) and measured by a flame ionization detector. The amount of CO<sub>2</sub> or CH<sub>4</sub> in a sample is directly proportional to the concentration of carbonaceous material in the sample.
- 2.3 Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, sample preparation and choice of analytical

instruments will determine which forms of carbon are actually measured. The forms of carbon that can be measured by the method are:

- Soluble, nonvolatile organic carbon: e.g., natural sugars
- Soluble, volatile organic carbon: e.g., mercaptans, alkanes, low molecular weight alcohols
- Insoluble, partially volatile carbon: e.g., low molecular weight oils
- Insoluble, particulate carbonaceous materials: e.g., cellulose fibers
- Soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter: e.g., oily matter adsorbed on silt particles

2.4 This is a quantitative analysis that qualitatively detects all organic carbon rather than a specific form or compound. The working range of the analysis is dependent upon the TOC analyzer and the range of working calibration standards used.

### 3.0 Interferences

3.1 Carbon is ubiquitous in nature, and so reagents, water, and glassware may not be cleaned completely of it. Positive bias may be caused by contaminants in the gas, dilution water, reagents, or glassware. Contamination introduced to the sample can be monitored through the use of reagent blanks, but there is no way to remove all carbon contamination.

3.2 Removal of carbonate and bicarbonate by acidification and purging with nitrogen or other inert gas can result in the loss of volatile organic substances.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

6.1 Total Organic Carbon Instrument: The most appropriate system should be selected based on consideration of the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured. No specific analyzer is recommended as superior. If the technique of chemical oxidation is used, the laboratory must demonstrate that the instrument is capable of achieving good carbon recoveries in samples containing particulates.

6.2 Blender for Homogenizing Samples: Waring-type blender or equivalent is satisfactory.

## 7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the TOC analyzer is performed according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Potassium Hydrogen Phthalate, Stock Solution: Weigh out 0.2128 gram of primary standard grade potassium hydrogen phthalate (previously dried to a constant weight at 110°C). Transfer standard to 100-mL volumetric flask, dilute to mark with water, and swirl to mix. This solution is stable for at least 3 weeks.

- 8.3 Potassium Hydrogen Phthalate, Working Standard Solutions: Prepare working standard solutions that bracket the expected sample concentration range by diluting stock solution.
- 8.4 Carbonate-Bicarbonate Stock Solution, 1,000 mg carbon/L: Weigh out 0.3500 gram of sodium bicarbonate and 0.4418 gram of sodium carbonate. Transfer both to the same 100-mL volumetric flask, dilute to mark with water, and swirl to mix.
- 8.5 Carbonate-Bicarbonate, Working Standard Solutions: Prepare working standard solutions that bracket the expected sample concentration range by diluting stock solution.
- 8.6 Potassium Persulfate Reagent ( $K_2S_2O_8$ ), 2% Solution: Dissolve 20 grams of reagent grade  $K_2S_2O_8$  in 50 mL of water. Add 2 mL of concentrated phosphoric acid and swirl to mix. Dilute to 1 liter. Store in a cool, dark location. This solution is stable for at least 1 month. **Caution:** Heat-liberating reaction.

## 9.0 Calibration Procedure

Calibrate TOC analyzer according to the manufacturer's directions. At least three calibration standards and one blank will be used to bracket the expected sample concentration range. Once the instrument has been calibrated, calibration is verified using a laboratory control sample.

## 10.0 Sample Preparation

Prepare samples according to the TOC instrument manufacturer's directions. All samples must be homogenized with the blender before sample analysis begins.

## 11.0 Sample Analysis

Analyze samples according to the TOC instrument manufacturer's directions. Analyze each sample in quadruplicate, and average the results to obtain the final reporting value. Report both the average concentration as well as the range of concentrations.

3203

**12.0 Calculations**

Calculations vary depending on the type of instrument selected and are detailed in the manufacturer's directions.

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 415.1. March 1983.

15.2 *Test Methods for Evaluating Solid Waste.* 3rd ed., SW-846. Method 9060.  
September 1986.

FERNALD/toc.51



## Alkalinity (Titrimetric)

**Working Linear Range:** All concentration ranges  
**Reporting Limit:** 1.0 mg/L  
**Reporting Units:** mg/L as CaCO<sub>3</sub>  
**Matrix:** Water and wastes

### 1.0 Scope and Application

- 1.1 The method is applicable to drinking, surface, and saline waters and domestic and industrial aqueous wastes.
- 1.2 The method is suitable for all concentration ranges of alkalinity. Appropriate aliquots should be used to avoid a titration volume greater than 50 mL.

### 2.0 Method Summary

An unaltered sample is titrated with a standard acid solution to a pH of 4.5 for total alkalinity. The endpoint may be determined electrometrically or with a color indicator. The sample must not be filtered, diluted, or altered in any way.

### 3.0 Interferences

- 3.1 By coating the pH electrode, oil and grease may interfere causing sluggish response. Allow sufficient time between titrant additions to allow electrodes to equilibrate. Clean electrodes occasionally.
- 3.2 For samples having high concentrations of mineral acids, such as mine wastes and associated receiving waters, titrate to an electrometric endpoint of pH 3.9.
- 3.3 Color indicators may not be used in the presence of interfering color and turbidity.
- 3.4 Salts of weak acids present in large amounts may cause interference with electrometric pH measurement.

3203

#### **4.0 Safety Precautions**

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these chemicals must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

- 6.1 pH Meter or electrically operated Titrator that uses a glass electrode and can be read to 0.05 pH unit (for electrometric determinations) with automatic temperature compensator.
- 6.2 Titration Vessel (Beaker, Erlenmeyer Flask).
- 6.3 Magnetic Stirrer and Teflon Stirring Bar.
- 6.4 Class A Volumetric Pipets.
- 6.5 Class A Burets: 50-, 25-, and 10-mL (in 0.1-mL increments).
- 6.6 Microburets: 1-mL (in 0.01-mL increments).
- 6.7 Class A Volumetric Flasks.

**7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the pH meter and the electrically operated titrator according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Standards**

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Standard Sodium Carbonate Solution ( $\text{Na}_2\text{CO}_3$ ), 0.05 N: Available commercially, or prepare as follows:
- 8.2.1 Dry 3 to 5 grams  $\text{Na}_2\text{CO}_3$  at  $250^\circ\text{C}$  for 4 hours and cool in a desiccator.
- 8.2.2 Add  $2.50 \pm 0.01$  grams of dried  $\text{Na}_2\text{CO}_3$  to a 1-liter volumetric flask.
- 8.2.3 Dilute to mark with water. This solution is stable for at least 1 week.
- 8.3 Standard Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), 0.02 N: Available commercially, or prepare as follows:
- 8.3.1 Add about 700 mL water to a 1-liter volumetric flask.
- 8.3.2 Slowly add 200 mL 0.100 N  $\text{H}_2\text{SO}_4$  to the flask and mix. **Caution:** Heat-liberating reaction.
- 8.3.3 Cool and dilute to the mark.
- 8.3.4 Standardize against 0.02 N  $\text{Na}_2\text{CO}_3$  solution (see step 9.1).
- 8.4 Standard Acid (Sulfuric or Hydrochloric), 0.1 N: Dilute 3.0 mL of concentrated  $\text{H}_2\text{SO}_4$  or 8.3 mL of concentrated HCl to 1 liter with water. **Caution:** Heat-liberating reaction. Standardize versus 40.0 mL of 0.02 N  $\text{Na}_2\text{CO}_3$  solution with about 60 mL water by titrating potentiometrically to pH of about 5. Lift electrode and rinse into beaker. Boil solution gently for

3 to 5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to pH inflection point. Calculate normality as:

$$N = \frac{A \times B}{53.00 \times C}$$

Where:

A	=	mass of $\text{Na}_2\text{CO}_3$ , weighed into 1 liter (grams)
B	=	volume of $\text{Na}_2\text{CO}_3$ solution (mL)
C	=	volume of acid used to inflection point (mL)

8.5 Bromocresol Green Indicator Solution, pH 4.5: Available commercially, or dissolve 100 mg bromocresol green, sodium salt, in 100 mL water.

## 9.0 Calibration Procedure

9.1 Standardizing Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), 0.02 N

9.1.1 If a pH meter is to be used to determine endpoint, calibrate according to instrument manufacturer's directions.

9.1.2 Using a volumetric pipet, measure 15 mL of standard 0.02 N  $\text{Na}_2\text{CO}_3$  solution into the titration vessel. Add 60 mL of water for a final volume of about 100 mL.

9.1.3 Use magnetic stirrer to stir sample gently while titrating.

9.1.4 Add 5 to 10 drops of bromocresol green. If using a pH meter to determine endpoint, this is not necessary but may be helpful.

9.1.5 Titrate with 0.02 N  $\text{H}_2\text{SO}_4$  titrant to the pH 4.5 endpoint. If using bromocresol green indicator, the endpoint is reached when the color changes from yellow to blue. If using pH meter, place electrodes in sample and measure pH. As standard acid is added, allow pH to equilibrate (stabilize). As the endpoint is approached, make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

9.1.6 Record volume (mL) of titrant used.

3203

9.1.7 Calculate normality of  $H_2SO_4$  using the calculation in step 12.1.

## 10.0 Sample Preparation

10.1 Allow sample to come to room temperature.

10.2 Mix the sample gently to obtain a representative sample before removing an aliquot for analysis.

## 11.0 Sample Analysis

11.1 For alkalinity above 20 mg/L  $CaCO_3$ :

11.1.1 Using a pipet, measure a volume of sample into the titration vessel and note the sample volume. Add water for a total volume of about 100 mL. For less than 1,000 mg  $CaCO_3/L$ , use 0.02 N titrant. For more than 1,000 mg  $CaCO_3/L$ , use 0.1 N titrant.

11.1.2 Use magnetic stirrer to gently stir sample while titrating.

11.1.3 Add 5 to 10 drops of bromcresol green. If using a pH meter to determine endpoint, this is not necessary, but may be helpful.

11.1.4 Titrate with  $H_2SO_4$  titrant to the pH 4.5 endpoint. If using bromcresol green indicator, the endpoint is reached when the color changes from yellow to blue. If using pH meter, titrate to pH 4.5. As standard acid is added, allow pH to equilibrate (stabilize). As the endpoint is approached, make smaller additions of acid and be sure that pH equilibrium is reached before adding more titrant.

11.1.5 Record volume (mL) of titrant used.

11.2 For low alkalinity (below 20 mg/L  $CaCO_3$ ):

11.2.1 Use 100 to 200 mL of sample and 0.02 N  $H_2SO_4$  using a 10-mL buret.

11.2.2 Stop titration at pH in range of 4.3 to 4.7, record volume and exact pH. Very carefully add titrant to lower pH exactly 0.3 unit and record volume.

3203

**12.0 Calculations**

12.1 For determining normality of standard acid:

$$N_2 = \frac{V_1 \times N_1}{V_2}$$

Where:

$N_2$	=	normality of $H_2SO_4$ titrant
$V_2$	=	volume of $H_2SO_4$ titrant used (mL)
$N_1$	=	normality of standard $Na_2CO_3$ (0.02 N)
$V_1$	=	volume of standard $Na_2CO_3$ (mL)

12.2 For total alkalinity above 20 mg/L  $CaCO_3$ :

$$\text{mg/L } CaCO_3 = \frac{A \times N \times 50,000}{\text{mL of sample}}$$

Where:

A	=	titrant (mL)
N	=	normality standard acid (titrant)

12.3 For low alkalinity below 20 mg/L  $CaCO_3$ :

$$\text{mg/L } CaCO_3 = \frac{(2B - C) \times N \times 50,000}{\text{mL of sample}}$$

Where:

B	=	volume of titrant to first recorded pH (mL)
C	=	total titrant to reach pH 0.3 unit lower (mL)
N	=	normality standard acid (titrant)

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Method 403. 1985.
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. March 1983. Method 310.1.



3203

## Alkalinity (Colorimetric)

**Working Linear Range:** 10 to 200 mg/L as CaCO<sub>3</sub>  
**Reporting Limit:** 10 mg/L as CaCO<sub>3</sub>  
**Reporting Units:** mg/L as CaCO<sub>3</sub>  
**Matrix:** Water and wastes

### 1.0 Scope and Application

- 1.1 This automated method is applicable to drinking, surface, and saline waters and domestic and industrial aqueous wastes. The applicable range is 10 to 200 mg/L as CaCO<sub>3</sub>.
- 1.2 The method is not approved for NPDES monitoring for samples containing turbidity or color.

### 2.0 Method Summary

Methyl orange is used as the indicator in the method because its pH range is in the same range as the equivalence point for total alkalinity and because it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.

### 3.0 Interferences

- 3.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. If the sample is filtered, the method is not approved for NPDES monitoring.
- 3.2 Sample color that absorbs in the photometric range used will also interfere.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the

procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

### **6.0 Apparatus**

- 6.1 Technicon Autoanalyzer (or equivalent) consisting of:
- 6.1.1 Sampler.
  - 6.1.2 Manifold.
  - 6.1.3 Proportioning pump.
  - 6.1.4 Colorimeter equipped with 15-mm tubular flow cell and 550-nm filters.
  - 6.1.5 Recorder equipped with range expander.

### **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the autoanalyzer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Methyl Orange: Dissolve 0.125 gram of methyl orange in 1 liter of water.

8.3 Buffer, pH 3.1: Available commercially, or prepare as follows:

8.3.1 Dissolve 5.1047 grams of potassium acid phthalate (KHP) in water.

8.3.2 Add 87.6 mL of 0.1 N hydrochloric acid (HCl) and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.3.3 This buffer is stable for at least 1 week (see step 9.1).

8.4 Methyl Orange Buffered Indicator

8.4.1 Add 1 liter of pH 3.1 buffer (step 8.3) to 200 mL methyl orange solution (step 8.2).

8.4.2 Mix well.

8.4.3 Solution is stable for at least 24 hours and should be prepared before each day of sample analysis.

8.5 Stock Standard Solution (1.0 mL = 1.00 mg CaCO<sub>3</sub>): Available commercially, or prepare as follows:

8.5.1 Dry 2 to 5 grams of anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) at 250°C for 4 hours.

8.5.2 Dissolve 1.060 grams dried anhydrous Na<sub>2</sub>CO<sub>3</sub> in water and swirl to mix.

8.5.3 Dilute to 1000 mL.

8.5.4 1.0 mL = 100 mg CaCO<sub>3</sub>.

8.6 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with water. The following dilutions are suggested:

mL of Stock Solution	Concentration mg/L as CaCO <sub>3</sub>
1.0	10
2.0	20
4.0	40
6.0	60
8.0	80
10.0	100
18.0	180
20.0	200

## 9.0 Calibration Procedures

- 9.1 Prepare at least four standards covering the working linear range of the samples (see step 8.5). Also prepare a calibration blank using ASTM Type II water.
- 9.2 Run the standard curve (four more standards plus the blank), and plot peak height as a function of concentration.
- 9.3 Immediately after the curve is prepared, analyze a continuous calibration verification sample to verify the calibration.

## 10.0 Sample Preparation

No advance sample preparation is required. Allow sample to warm to room temperature.

## 11.0 Sample Analysis

- 11.1 Set up manifold according to the manufacturer's direction.
- 11.2 Allow both colorimeter and recorder to warm up for about 30 minutes. Run a baseline with all reagents while feeding water through the sample line. Adjust colorimeter to obtain a stable baseline.
- 11.3 Place water wash tubes in alternate openings on sampler and set sample timing to 2 minutes.

- 11.4 Place working standards in sampler in order of decreasing concentration. Fill sampler tray completely with quality control samples and unknown samples.
- 11.5 Switch sample line from water to sampler and begin analysis.

## 12.0 Calculations

Compute concentration of samples by comparing sample peak heights with the standard curve (see step 9.2).

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

## 15.0 References

U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB8-4-128677.  
Method 310.2. March 1983.

FERNALD/alk-col.51

## pH (Electrometric)

**Working Linear Range:** 0 to 14  
**Reporting Limit:** N/A  
**Reporting Units:** pH units  
**Matrix:** Water and wastes

### 1.0 Scope and Application

This method is applicable to drinking, surface, ground, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.

### 3.0 Interferences

- 3.1 Coatings of oily material or particulate material can impair electrode response. Remove coatings by gentle wiping or detergent washing followed by ASTM Type II water rinse and additional treatment with hydrochloric acid (1:10) to remove any remaining film.
- 3.2 Temperature errors are sample-dependent and cannot be controlled. Note both pH and temperature at the time of analysis, and correct the pH for temperature effects if required.
- 3.3 A sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium-error" electrode.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.



3203

## **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## **6.0 Apparatus**

- 6.1 Laboratory pH Meter: Commercially available, preferably equipped with automatic temperature compensation.
- 6.2 Reference and pH Sensing Electrodes, or a combination electrode: Commercially available.
- 6.3 Magnetic Stirrer and Teflon-coated Stirring Bar.
- 6.4 Thermometer and Temperature Sensor for automatic compensation.
- 6.5 Beakers: Preferably polyethylene or Teflon.

## **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the pH meter and electrodes according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## **8.0 Reagents and Calibration Standards**

- 8.1 NIST-traceable standard buffers are available commercially. At least two buffers about 3 pH units apart are required for calibration.
  - 8.1.1 It is suggested that buffers of pH 4, 7, and 10 be used for calibration.
- 8.2 Water: All references to water assume the use of ASTM Type II water.

8.3 Hydrochloric acid, HCl: 1 to 10 dilution.

## 9.0 Calibration Procedure

9.1 Calibrate pH meter according to manufacturer's directions.

9.2 The pH must be calibrated at a minimum of two points that bracket the expected pH of the samples and are three pH units or more apart. The third buffer may be used as a QC check sample. The reading of the buffer should be within 0.1 pH unit of the true pH.

## 10.0 Sample Preparation

Mix the sample gently before removing a representative aliquot.

## 11.0 Sample Analysis

11.1 Calibrate the pH meter according to the manufacturer's directions.

11.2 Place the sample in a clean beaker of adequate size for the electrode and the stirring bar. Sample aliquot should be sufficient to cover the tip of the electrode completely.

11.3 Measure and record sample temperature.

11.4 After rinsing and gently wiping electrodes, immerse them into sample beaker and stir at constant rate. Rate of stirring should provide homogeneity and suspension of solids, but should minimize air transfer at the air/water interface.

11.5 Record pH reading.

11.6 If sample temperature differs by more than 2°C from buffer solution, measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's directions.

11.7 Repeat measurement on successive volumes of samples until values differ by less than 0.1 pH unit.

3203

**12.0 Calculations**

- 12.1 Report pH results to nearest 0.1 pH unit.
- 12.2 Report temperature results to nearest 1°C.

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90-110%	Recalibrate
CCVS	1/20	90-110%	Recalibrate
LCS	Begin	80-120%	Recalibrate
Duplicate Sample	1/20	0-20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference

**15.0 References**

- 15.1 APHA et al. *Standard Method for the Examination of Water and Wastewater*. 16th ed., Method 423. 1985.
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 150.1. March 1983.

15.3 *Test Methods for Evaluating Solid Waste.* SW846. Method 9040. September 1986.

FERNALD/ph.51



## Chloride (Colorimetric, Automated Ferricyanide)

**Working Linear Range:** 1.0 to 200 mg/L  
**Reporting Limit:** 1.0 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and wastes

### 1.0 Scope and Application

This automated method is applicable to drinking, surface, saline, and ground waters and domestic and industrial wastes. The applicable range is 1 to 200 mg Cl<sup>-</sup> per liter of sample. The range can be extended by diluting the sample.

### 2.0 Method Summary

Thiocyanate ion (SCN) is liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form un-ionized mercuric chloride. In the presence of ferric ion, the liberated SCN forms highly colored ferric thiocyanate in a concentration proportional to the original chloride concentration.

### 3.0 Interferences

There are no significant interferences.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## **6.0 Apparatus**

### **6.1 Automated Continuous-flow Analytical Instrument.**

#### **6.1.1 Sampler.**

#### **6.1.2 Analytical Cartridge.**

#### **6.1.3 Proportioning Pump.**

#### **6.1.4 Colorimeter: Equipped with 15-mm tubular flowcell and 480-nm filters.**

#### **6.1.5 Recorder.**

#### **6.1.6 Digital Printer (optional).**

## **7.0 Routine Preventive Maintenance**

### **7.1 Perform routine preventive maintenance for the continuous-flow analytical instrument according to the manufacturer's directions.**

### **7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.**

### **7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.**

## **8.0 Reagents and Calibration Standards**

### **8.1 Water: All references to water assume the use of ASTM Type II water.**

### **8.2 Mercuric Thiocyanate Solution: Dissolve 4.17 grams of $\text{Hg}(\text{SCN})_2$ in 500-mL methanol. Dilute to 1 liter with methanol, mix, and filter through Whatman #40 filter paper or equivalent.**

3203

- 8.3 Ferric Nitrate Solution, 20.2%: Dissolve 202 grams of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 500 mL of water. Add 31.5 mL concentrated nitric acid, mix, and dilute to 1 liter with water. **Caution:** Heat-liberating reaction.
- 8.4 Color Reagent: Commercially available. To prepare, add 150 mL of mercuric thiocyanate solution to 150 mL of ferric nitrate solution, mix, and dilute to 1 liter with water.
- 8.5 Sodium Chloride Stock Solution (NaCl), 0.0141 N: Dissolve 0.8241 gram of predried (dried in a 140°C oven for at least 1 hour) NaCl in water. Dilute to 1 liter in a volumetric flask (1 mL = 0.5 mg Cl<sup>-</sup>).
- 8.5.1 Prepare a series of working standards by diluting suitable volumes of stock solution to 100 mL with water. The following dilutions are suggested, and it is not necessary to prepare all the solutions:

Stock Solution (mL)	Concentration (mg/L)
1.0	5.0
2.0	10.0
4.0	20.0
8.0	40.0
15.0	75.0
20.0	100.0
30.0	150.0
40.0	200.0

## 9.0 Calibration Procedures

- 9.1 Prepare at least four standards bracketing the expected range of the samples and one calibration blank.
- 9.2 Analyze the standard solutions and the blank. Prepare a standard curve by plotting a peak height as a function of concentration.
- 9.3 Immediately after standard curve is prepared, analyze laboratory control sample (LCS) to verify calibration. Acceptance criteria for the LCS will be 90 to 110% or limits established by laboratory-specific control charts, whichever range is smaller.

- 9.4 A continuing calibration verification sample (CCVS) and a continuing calibration blank should be analyzed after every 10 samples or after every analytical batch, whichever is more frequent. The recommended acceptance criteria for CCVS is 90 to 110% recovery.

#### **10.0 Sample Preparation**

If particulate matter is visible, the sample must be filtered or centrifuged before analysis.

#### **11.0 Sample Analysis**

- 11.1 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents feeding water through the sample line, as specified by the instrument manufacturer's directions.
- 11.2 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with LCSs and unknown samples.
- 11.3 When a stable baseline has been obtained, start sampler as specified by instrument manufacturer's directions.

#### **12.0 Calculations**

Compute concentration of samples by comparing sample peak heights with standard curve. Note that the curve will probably be non-linear.

#### **13.0 Data Package Deliverables**

Data package deliverables are determined by Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/10	90–110%	Recalibrate
LCS	Begin	90–110%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

## 15.0 References

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 325.2. March 1983.
- 15.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed., SW 846. Method 9251. September 1986.



## Sulfide

**Working Linear Range:** Infinite with dilution  
**Reporting Limit:** 1 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water

### 1.0 Scope and Application

- 1.1 The method applies to the measurement of total sulfides in drinking, surface, saline, and ground waters. The applicable range is infinite with proper dilutions.
- 1.2 Acid-insoluble sulfides are not measured by this test. (Copper sulfide is the only common sulfide in this class.)

### 2.0 Method Summary

Excess iodine is added to a water sample that has been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is backtitrated with sodium thiosulfate.

### 3.0 Interferences

Reduced sulfur compounds such as sulfite, thiosulfate, and hydrosulfite that decompose in acid may yield erratic results. Volatile iodine-consuming substances will give high results.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during this method, procedures for handling these compounds must be practiced. Personal protective equipment

must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## **6.0 Apparatus**

- 6.1 Class A Burets.
- 6.2 Flasks and Beakers.
- 6.3 Class A Volumetric Flasks.

## **7.0 Routine Preventive Maintenance**

Examine glassware before each use for scratches and cracks, and replace as necessary.

## **8.0 Reagents and Calibration Standards**

- 8.1 Hydrochloric Acid (HCl), 6 N.
- 8.2 Water: All references to water assume the use of ASTM Type II water.
- 8.3 Standard Iodine Solution, 0.0250 N.
  - 8.3.1 Dissolve 20 to 25 grams KI in a small amount of water in a 1-liter volumetric flask, and add 3.2 grams iodine. Swirl to dissolve completely.
  - 8.3.2 Dilute to 1 liter with water. 1 mL reacts with 0.4 mg of sulfide.
  - 8.3.3 Standardize against 0.0250 N sodium thiosulfate using starch indicator.
  - 8.3.4 The solution is not stable and should be standardized each day of use.

8.4 Sodium Thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ), 0.0250 N: Commercially available.

8.4.1 Dissolve 6.205 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in water. Add 1.5 mL of 6 N NaOH and dilute to 1 liter.

8.4.2 Standardize with bi-iodate solution.

8.5 Standard Potassium Bi-iodate Solution ( $\text{KH}(\text{IO}_3)_2$ ), 0.0021 M.

8.5.1 Dissolve 812.4 mg  $\text{KH}(\text{IO}_3)_2$  in water and dilute to 1 liter.

8.5.2 Dissolve 2 grams KI, free of iodate, in an Erlenmeyer flask with 100 to 150 mL of water.

8.5.3 Add 1 mL 6 N  $\text{H}_2\text{SO}_4$  and 20 mL standard bi-iodate solution. **Caution:** Heat-liberating reaction.

8.5.4 Dilute to 200 mL and titrate liberated iodine with thiosulfate titrant, adding starch toward end of titration, when a pale straw color is reached.

8.6 Starch Indicator: Commercially available.

8.7 Sodium Hydroxide, 0.25 N.

8.7.1 Dissolve 10 grams NaOH in a 1-liter volumetric flask.

8.7.2 Dilute to volume with water.

## 9.0 Calibration Procedures

Calibration is not required.

## 10.0 Sample Preparation

Sample preparation is not required.

## 11.0 Sample Analysis

11.1 Place 200 mL of water sample in a 500-mL flask.

- 11.2 Add starch indicator and known amount of iodine solution estimated to be in excess of the expected amount of sulfide.
- 11.3 Add 2 mL of 6 N HCl.
- 11.4 If iodine color disappears, add more iodine (and record the volume) until the color remains for more than 5 minutes after mixing.
- 11.5 Titrate with 0.025 N sodium thiosulfate until blue color disappears, and record total volume of titrant used.

## 12.0 Calculations

$$\text{mg/L sulfide} = \frac{[(A \times B) - (C \times D)] \times 16,000}{\text{mL sample}}$$

Where:

- A = volume of iodine solution (mL)  
B = normality of iodine solution  
C = volume Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution (mL)  
D = normality of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

3203

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 *Methods for Chemical Analysis of Water and Wastes*. PB84. Method 376.1. March 1983.
- 15.2 *Standard Methods for the Examination of Water and Wastewater*. 17th ed., Method 4500-S<sup>2</sup>E. 1989.

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3203

## Ammonia

**Working Linear Range:** 1.0 to 25 mg NH<sub>3</sub>-N/L  
**Reporting Limit:** 1.0 mg NH<sub>3</sub>-N/L  
**Reporting Units:** mg NH<sub>3</sub>-N/L  
**Matrix:** Water

### 1.0 Scope and Application

The method is applicable to measurement of ammonia in surface, saline, and ground waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

The sample is buffered at a pH of 9.5 with a borate buffer to decrease hydrolysis of cyanates and organic nitrogen compounds, and is then distilled into a solution of boric acid. The concentration of ammonia in the distillate is determined titrimetrically with standard sulfuric acid using a mixed indicator.

### 3.0 Interferences

Residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these chemicals must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

6.1 Distillation Apparatus: Commercially available as a unit and made of all borosilicate glass, equipped with a 800- to 1,000-mL distillation flask.

6.2 Titration Vessels: Beakers or Erlenmeyer flasks.

6.3 Magnetic Stirrer and Teflon Stirring Bar.

6.4 Class A Volumetric Glassware, including pipets and burets.

6.5 pH Meter.

6.6 Boiling Chips.

## 7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the pH meter according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Stock Sulfuric Acid Solution ( $\text{H}_2\text{SO}_4$ ) 0.1 N: Dilute 3.0 mL concentrated  $\text{H}_2\text{SO}_4$  to 1 liter with water. **Caution:** Heat-liberating reaction.

8.3 Standard Sulfuric Acid Titrant, 0.02 N: Available commercially or prepared as follows:

- 8.3.1 Add approximately 700 mL of water to a 1-liter volumetric flask.
- 8.3.2 Add 200 mL of 0.100 N  $\text{H}_2\text{SO}_4$  to the flask and swirl to mix. **Caution:** Heat-liberating reaction.
- 8.3.3 Cool and dilute to mark with water.
- 8.3.4 Standardize against 0.02 N  $\text{Na}_2\text{CO}_3$  solution as described in Section 9.
- 8.4 Standard Sodium Carbonate Solution ( $\text{Na}_2\text{CO}_3$ ), 0.02 N: Available commercially or prepared fresh weekly as follows:
- 8.4.1 Dry 2 to 3 grams  $\text{Na}_2\text{CO}_3$  at 250°C for 4 hours and cool in a desiccator.
- 8.4.2 Add 1.060 grams of dried  $\text{Na}_2\text{CO}_3$  to a 1-liter volumetric flask.
- 8.4.3 Dilute to mark with water.
- 8.5 Bromocresol Green Indicator Solution, pH 4.5: Available commercially, or prepare by dissolving 100 mg bromocresol green, sodium salt, in 100 mL of water.
- 8.6 Sodium Hydroxide Solution, 6.0 N: To prepare, place approximately 500 mL of water in a 1-liter volumetric flask. Add 240.0 grams of NaOH and swirl to mix. Allow solution to cool and dilute to mark with water.
- 8.7 Sodium Hydroxide Solution, 0.1 N: Available commercially. To prepare, place approximately 500 mL of water in a 1-liter volumetric flask. Add 4.0 grams of NaOH and swirl to mix. Dilute to mark with water.
- 8.8 Mixed Indicator Solution: Dissolve 200 mg methyl red indicator in 100 mL 95% ethyl or isopropyl alcohol. Dissolve 100 mg methylene blue in 50 mL 95% ethyl or isopropyl alcohol. Combine solutions and store in tightly stoppered container. This solution is stable for at least 30 days.
- 8.9 Boric Acid Solution: Place approximately 600 mL of water in a 1-liter volumetric flask. Add 20 grams  $\text{H}_3\text{BO}_3$  and swirl to mix. Add 10 mL mixed indicator solution. Dilute to mark with water. Prepare monthly.

3203

**8.10 Borate Buffer**

- 8.10.1 Prepare sodium tetraborate solution, 0.025 M. Place approximately 500 mL of water in a 1-liter volumetric flask. Add either 5.0 grams anhydrous sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ) or 9.5 grams hydrated sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) and swirl to mix. Dilute to mark with water.
- 8.10.2 Transfer 500 mL of 0.025 M sodium tetraborate solution to a 1-liter volumetric flask. Add 88 mL of 0.1 N NaOH solution and swirl to mix. Dilute to mark with water.
- 8.11 Dechlorinating Agent: Dissolve 3.5 grams of sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in 1 liter of water. 1 mL of solution will remove 1 mg/L of residual chlorine in a 500-mL sample.

**9.0 Calibration Procedures****9.1 Standardizing  $\text{H}_2\text{SO}_4$** 

- 9.1.1 If a pH meter is to be used to determine the endpoint, calibrate meter according manufacturer's directions.
- 9.1.2 Using volumetric pipet, measure 40 mL of standard 0.02 N  $\text{Na}_2\text{CO}_3$  solution into titration vessel. Add 60 mL of water for a final volume of approximately 100 mL.
- 9.1.3 Gently place Teflon stirring bar into flask and turn on magnetic stirrer to stir sample gently while titrating.
- 9.1.4 Add 5 to 10 drops of bromocresol green. If using a pH meter to determine the endpoint, this is not necessary but may be helpful.
- 9.1.5 Titrate with  $\text{H}_2\text{SO}_4$  titrant to pH 4.5 endpoint. If using bromocresol green indicator, endpoint is reached when color changes from yellow to blue. If using a pH meter, place electrodes in sample and measure pH. As acid is added, allow pH to stabilize. As endpoint is approached, make smaller additions of acid and be sure that pH equilibration is reached before adding more titrant.
- 9.1.6 Record volume of titrant used and calculate the normality of  $\text{H}_2\text{SO}_4$  solution.

**10.0 Sample Preparation**

- 10.1 Allow sample to come to room temperature.
- 10.2 Remove residual chlorine in sample by adding dechlorinating agent equivalent to chlorine residual.
- 10.3 Check pH of solution using either pH meter or short-range pH paper, and then adjust pH to 9.5 using 6 N NaOH.
- 10.4 Transfer 500 mL of sample to distillation flask and add 25 mL of borate buffer solution.

**11.0 Sample Analysis**

- 11.1 Assemble distillation apparatus according to manufacturer's directions.
- 11.2 Add 500 mL of water and 20 mL borate buffer to distillation flask and adjust pH of solution to 9.5 with 6 N NaOH. Add a few boiling chips and use mixture to steam out distillation apparatus until distillate shows no traces of ammonia.
- 11.3 To minimize contamination, leave distillation apparatus assembled after steaming out and until just before starting sample distillation. Disconnect steaming-out flask and immediately transfer sample flask to distillation apparatus. Replace distillate collection flask with a clean flask containing 50 mL of indicating boric acid solution. Distill at a rate of 6 to 10 mL/min with tip of delivery tube below surface of acid receiving solution. Collect at least 200 mL of distillate. Lower collected distillate free of contact with delivery tube and continue distillation during the last few minutes to cleanse condenser and delivery tube. Dilute to 500 mL with water.
- 11.4 Determine concentration of ammonia in distillate by titration with standard 0.02 N H<sub>2</sub>SO<sub>4</sub> until solution turns pale lavender. Compare color endpoint against a blank containing the same volume of distilled water and H<sub>3</sub>BO<sub>3</sub> solution (not the method blank).

## 12.0 Calculations

12.1 The normality of standard H<sub>2</sub>SO<sub>4</sub> acid solution is:

$$N_2 = \frac{(V_1) (N_1)}{V_2}$$

Where:

N <sub>2</sub>	=	normality of H <sub>2</sub> SO <sub>4</sub>
V <sub>1</sub>	=	volume of standard Na <sub>2</sub> CO <sub>3</sub> (mL)
N <sub>1</sub>	=	normality of standard Na <sub>2</sub> CO <sub>3</sub> solution (0.02 N)
V <sub>2</sub>	=	volume of standard H <sub>2</sub> SO <sub>4</sub> (mL)

12.2 The concentration of ammonia is:

$$\text{mg NH}_3\text{-N/L} = \frac{(280) (A - B)}{\text{mL sample}}$$

Where:

A	=	0.02 N H <sub>2</sub> SO <sub>4</sub> used for titration (mL)
B	=	blank correction (mL of 0.02 N H <sub>2</sub> SO <sub>4</sub> used for titrating method blank)

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

#### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

#### 15.0 References

- 15.1 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Method 403. 1985.
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 350.2. March 1983.



3203

## Hexavalent Chromium (Cr<sup>6+</sup>)

**Working Linear Range:** 10 to 250  $\mu\text{g/L}$   
**Reporting Limit:** 10  $\mu\text{g/L}$   
**Report Units:**  $\mu\text{g/L}$   
**Matrix:** Water

### 1.0 Scope and Application

The method covers the determination of dissolved hexavalent chromium in drinking, surface, and saline waters. It may be applicable to some domestic and industrial aqueous wastes.

### 2.0 Method Summary

Only hexavalent chromium is measured using the method. Hexavalent chromium in a sample is determined colorimetrically by reaction with diphenylcarbazide in acid solution, which produces a violet color of unknown composition.

### 3.0 Interferences

The reaction with diphenylcarbazide is nearly specific for chromium. Hexavalent molybdenum and mercury salts will react to form color with the reagent, but the intensities are much lower than that for chromium at the specified pH. Concentrations as high as 200 mg/L of molybdenum or mercury do not cause significant interference. Vanadium interferes when present in concentrations greater than 10 times the concentration of chromium. Iron in concentrations greater than 1 mg/L may produce a yellow color but does not interfere if the absorbance of hexavalent chromium is measured at the specified wavelength.

### 4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

### 6.0 Apparatus

- 6.1 Spectrophotometer: Double-beam unit for use at 540 nm with a light path of 1 cm or longer.
- 6.2 Separatory Funnels: 125-mL, with glass or Teflon stopcocks and stoppers.
- 6.3 pH Meter.

### 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the spectrophotometer and pH meter according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

### 8.0 Reagents and Calibration Standards

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Stock Chromium Solution: Place approximately 500 mL of water in 1-liter volumetric flask. Add 141.4 mg  $K_2Cr_2O_7$  and swirl to mix. Dilute to mark with water. 1 mL = 50.0  $\mu$ g Cr.

- 8.3 Standard Chromium Solution: Dilute 10.0 mL stock chromium solution to 100 mL. 1 mL = 5.00  $\mu\text{g}$  Cr.
- 8.4 Nitric Acid ( $\text{HNO}_3$ ): Concentrated.
- 8.5 Diphenylcarbazide Solution: Place approximately 50 mL of acetone in 50-mL volumetric flask. Add 250 mg 1,5-diphenylcarbazide and swirl to mix. Dilute to mark with acetone and store in brown bottle out of light. Solution must be discarded when it discolors.
- 8.6 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), 0.02 N: Place approximately 300 mL water in 500-mL volumetric flask. Add 17.0 mL of 6 N  $\text{H}_2\text{SO}_4$  and swirl to mix. **Note:** Heat-liberating reaction. When cool, dilute to mark with water.

### 9.0 Calibration Procedures

- 9.1 Prepare calibration solutions using standard chromium solution. It is not necessary to prepare all solutions—only four points that bracket the expected sample concentration range and one blank are needed. Using 250-mL beakers or conical flasks:

Standard Solution (mL)	Final Concentration (mg/L)
0.0	0.0
1.0	5.0
2.0	10.0
5.0	25.0
10.0	50.0
20.0	100.0

- 9.2 The standard solutions are prepared in the same manner as samples. Once absorbance of each solution has been measured, a calibration curve is prepared by plotting absorbance as a function of concentration.

### 10.0 Sample Preparation

Sample preparation is not required.

3203

**11.0 Sample Analysis**

- 11.1 Check pH of solution with pH meter. Adjust pH of solution to < 1 with 0.02 N H<sub>2</sub>SO<sub>4</sub>.
- 11.2 Transfer solution to 100-mL volumetric flask and dilute to mark with water.
- 11.3 Add 2.0 mL diphenylcarbazide solution, mix, and let stand 5 to 10 minutes for color to develop. Swirl to mix.
- 11.4 Measure absorbance of sample at 540 nm.
- 11.5 Repeat process (steps 11.1 and 11.2) with a method blank.

**12.0 Calculation**

Hexavalent chromium is calculated as:

$$\text{mg Cr}^{+6}/\text{L} = \frac{\mu\text{g Cr} (\in 102 \text{ mL final volume}) (100)}{(A) (B)}$$

Where:

- A = original sample (mL)  
B = aliquot of sample analyzed (mL)

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

#### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

#### 15.0 Reference

*Standard Methods for Examination of Water and Wastes.* 17th ed., Method 3500-Cr D. 1989.



## Temperature

<b>Working Linear Range:</b>	Thermometer-dependent
<b>Reporting Limit:</b>	Thermometer-dependent
<b>Reporting Unit:</b>	°C
<b>Matrix:</b>	Water and waste

### 1.0 Scope and Application

This method is applicable to drinking, surface, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

Temperature measurements may be made with any good grade of mercury-filled or dial type centigrade thermometer or a thermistor. Measurement device should be routinely checked against a precision thermometer certified by the NIST. At a minimum, the thermometer should have a scale marked for every 0.1°C, with markings etched on the capillary glass. The thermometer should have a minimal thermal capacity to permit rapid equilibration. Temperature measurements are often made in conjunction with other methods.

### 3.0 Interferences

None, unless the temperature falls outside the range of the thermometer.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

## **5.0 Sample Handling and Preservation**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## **6.0 Apparatus**

6.1 Thermometer.

6.2 Thermometer certified by the NIST for the temperature range of interest.

## **7.0 Routine Preventive Maintenance**

7.1 Perform routine preventive maintenance for the thermometer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

## **8.0 Reagents and Calibration Standards**

None. The thermometer is a self-contained piece of equipment.

## **9.0 Calibration Procedure**

Check the temperature of the thermometer against the NIST-traceable thermometer annually or more frequently as needed.

## **10.0 Sample Preparation**

Prepare sample as required for the corresponding analytical method.

## **11.0 Sample Analysis**

Make readings with the thermometer in the sample long enough to permit equilibration. Report results to the nearest 0.1° or 1.0°C, depending on need.

Thermometer must be cleansed between readings to avoid cross-contamination of samples.

## 12.0 Calculations

If the thermometer reading required correction after comparison to the certified thermometer:

$$T_{\text{actual}} = T - C$$

Where:

$T_{\text{actual}}$	=	actual temperature after correction (°C)
$T$	=	measured temperature (°C)
$C$	=	degrees of correction as indicated by the certified thermometer (°C)

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the corresponding analytical methods or the project-specific Sampling and Analysis Plan.

## 15.0 References

- 15.1 *Standard Methods for the Examination of Water and Wastewater*. 16th ed, Method 212. 1985.
- 15.2 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 170.1. March 1983.

FM-CON-0170

## Chloride (Titrimetric, Mercuric Nitrate)

**Working Linear Range:** All concentration ranges

**Reporting Limit:** 1.0 mg/L

**Reporting Units:** mg/L

**Matrix:** Water and wastes

### 1.0 Scope and Application

1.1 The method is applicable to drinking, surface, saline, and ground waters and domestic and industrial aqueous wastes.

1.2 The method is suitable for all concentration ranges of chloride content. To avoid large titration volumes, a sample aliquot containing not more than 10 to 20 mg Cl per 50 mL should be used.

1.3 Automated titration may be used.

### 2.0 Method Summary

An acidified sample is titrated with mercuric nitrate in the presence of mixed diphenylcarbazone-bromophenol blue indicator. The end point of the titration is the formation of the blue-violet mercury diphenylcarbazone complex.

### 3.0 Interferences

3.1 Anions and cations at concentrations normally found in surface waters do not interfere. However, at the higher concentration often found in certain wastes, problems may occur.

3.2 Sulfite interference can be eliminated by oxidizing the 50 mL of sample solution with 0.5 to 1 mL of hydrogen peroxide ( $H_2O_2$ ).

#### **4.0 Safety Precautions**

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling nitric acid, sodium hydroxide, and hydrogen peroxide must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

Standard laboratory titrimetric equipment, including 1- or 5-mL Class A microburets with 0.01-mL graduations.

#### **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the titrimetric equipment according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.
- 7.4 Clean and maintain microburets following the manufacturer's directions for routine cleaning and care.

3203

**8.0 Reagents and Calibration Standards**

- 8.1 Water: All references to water assume the use of ATSM Type II water.
- 8.2 Standard Sodium Chloride Solution, 0.025 N: Available commercially. To prepare, dissolve  $1.4613 \pm 0.0002$  gram of sodium chloride (dried at  $600^{\circ}\text{C}$  for 1 hour) in water in a 1-liter volumetric flask, and dilute to mark.  $1 \text{ mL} = 886.5 \mu\text{g Cl}$ .
- 8.3 Nitric Acid Solution ( $\text{HNO}_3$ ) (3 + 997): Place approximately 700 mL water in a 1-liter volumetric flask. Add 3 mL concentrated nitric acid and swirl to mix. **Caution:** Heat-liberating reaction. Dilute to mark.
- 8.4 Sodium Hydroxide Solution ( $\text{NaOH}$ ), 10 g/L: Dissolve approximately 10 grams of  $\text{NaOH}$  in water and dilute to 1 liter.
- 8.5 Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ): 30% solution available commercially.
- 8.6 Hydroquinone Solution, 10 g/L: Dissolve 1 gram of purified hydroquinone in water in a 100-mL volumetric flask and dilute to mark.
- 8.7 Mercuric Nitrate Titrant ( $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ), 0.0141 N: Available commercially, or prepare as follows. Place approximately 900 mL of water in a 1-liter volumetric flask. Add 0.25 mL of concentrated  $\text{HNO}_3$  and swirl to mix. Then add 2.4200 grams  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . Swirl until all solids are dissolved or filter if necessary. Dilute to nearly 1 liter and standardize against standard sodium chloride solution as outlined in Section 9.2. Store in dark bottle.
- 8.8 Mercuric Nitrate Titrant ( $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ), 0.025 N: Available commercially, or prepare as follows. Place approximately 50 mL of water in a 1-liter volumetric flask. Add 0.5 mL of concentrated  $\text{HNO}_3$  and swirl to mix. **Caution:** Heat-liberating reaction. Then add 4.283 grams  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . Swirl until all solids are dissolved or filter if necessary. Dilute to nearly 1 liter and standardize against standard sodium chloride solution as outlined in Section 9.2. Store in dark bottle.
- 8.9 Mercuric Nitrate Titrant ( $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ), 0.141 N: Available commercially, or prepare as follows. Place approximately 900 mL of water in a 1-liter volumetric flask. Add 5.0 mL of concentrated  $\text{HNO}_3$  and swirl to mix. **Caution:** Heat-liberating reaction. Then add 24.2 grams

$\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . Swirl until all solids are dissolved, or filter if necessary. Dilute to nearly 1 liter and standardize against standard sodium chloride solution as outlined in Section 9.2. Store in dark bottle.

- 8.10 **Mixed Indicator Reagent:** Place approximately 75 mL of 95% ethanol in a 100-mL volumetric flask. Add 0.5 gram crystalline diphenylcarbazone and 0.05 gram bromophenol blue powder, and swirl to mix. Dilute to mark with 95% ethanol. Store in dark bottle in refrigerator. This solution is stable for at least 6 months.
- 8.11 **Alphazurine Indicator Solution:** Dissolve 0.005 gram of alphazurine blue-green dye in 95% ethanol or isopropanol in 100-mL volumetric flask, and dilute to the mark with 95% ethanol or isopropanol.

## 9.0 Calibration Procedures

- 9.1 Because this is a titration procedure, there is no instrument to calibrate. The mercuric nitrate solution ( $\text{Hg}(\text{NO}_3)_2$ ), however, must be standardized against the standard sodium chloride solution.
- 9.2 Pipet appropriate volume of standard NaCl solution into clean titration vessel. Use Class A volumetric pipet to measure NaCl solution.
- 0.141 N  $\text{Hg}(\text{NO}_3)_2$ ; titrate 50 mL 0.025 N NaCl  
0.025 N  $\text{Hg}(\text{NO}_3)_2$ ; titrate 10 mL 0.025 N NaCl  
0.0141 N  $\text{Hg}(\text{NO}_3)_2$ ; titrate 5 mL 0.025 N NaCl
- 9.3 Add 5 to 10 drops of mixed indicator reagent, and swirl solution to mix.
- 9.4 If blue-violet or red color appears, add  $\text{HNO}_3$  solution dropwise until color changes to yellow.
- 9.5 Add 1 mL excess  $\text{HNO}_3$  solution.
- 9.6 Titrate with mercuric nitrate titrant until blue-violet color persists throughout solution.
- 9.7 Record volume (mL) of titrant used.
- 9.8 Calculate normality of  $\text{Hg}(\text{NO}_3)_2$  using the equation in Section 12.1.

**10.0 Sample Preparation**

- 10.1 Allow sample to equilibrate at ambient temperature.
- 10.2 Mix sample gently to ensure a representative sample before removing an aliquot for analyses.

**11.0 Sample Analysis**

- 11.1 Choose appropriate mercuric nitrate titrant concentration and sample aliquot volume.
- 11.1.1 If concentration is  $< 2.5$  mg Cl/L, use 0.0141 N mercuric nitrate titrant to titrate 50 mL of sample.
- 11.1.2 If concentration is  $> 2.5$  but  $< 20$  mg Cl/L, use 0.025 N mercuric nitrate titrant to titrate 50 mL of sample.
- 11.1.3 If concentration is  $> 20$  mg Cl/L sample, use 0.141 N mercuric nitrate titrant to titrate 50 mL of sample. Smaller sample volume can be titrated if more than 50 mL of mercuric nitrate titrant is needed.
- 11.2 Add 5 to 10 drops of mixed indicator reagent; swirl solution to mix.
- 11.3 If blue-violet or red color appears, add  $\text{HNO}_3$  solution dropwise until color changes to yellow.
- 11.4 If yellow or orange color forms immediately on addition of mixed indicator, add NaOH solution dropwise until color changes to blue-violet; then add  $\text{HNO}_3$  solution dropwise until color changes to yellow.
- 11.5 Add 1 mL excess  $\text{HNO}_3$  solution.
- 11.6 Titrate with mercuric nitrate titrant chosen in section 11.1 until a blue-violet color persists throughout the solution. If volume of titrant  $> 10$  mL use the 0.141 N mercuric nitrate solution; if  $< 1$  mL, use 0.0141 N. If necessary, titrate a small sample aliquot. Alphazurine indicator solution may be added with the indicator to sharpen the end point, which may change the color shades. Practice runs should be made.

- 11.6.1 If chromate is present at < 100 mg/L and iron is not present, add 5 to 10 drops of alphasurine indicator solution and acidify to a pH of 3 (measure with appropriate indicating paper). End point will then be an olive-purple color.
- 11.6.2 If chromate is present at > 100 mg/L and iron is not present, add 2 mL of fresh hydroquinone solution.
- 11.6.3 If ferric iron is present, use a sample volume containing no more than 2.5 mg of ferric ion or ferric ion plus chromate ion and add 2 mL fresh hydroquinone solution.
- 11.6.4 If sulfite ion is present, add 0.5 mL of H<sub>2</sub>O<sub>2</sub> solution to 50-mL sample and stir or swirl for 1 minute.
- 11.6.5 Repeat the entire procedure with water as a method blank.

## 12.0 Calculations

- 12.1 For determining normality of standard Hg(NO<sub>3</sub>)<sub>2</sub> titrant:

$$N_2 = \frac{V_1 \times N_1}{V_2}$$

Where:

N <sub>2</sub>	=	normality of Hg(NO <sub>3</sub> ) <sub>2</sub> titrant
V <sub>2</sub>	=	volume of Hg(NO <sub>3</sub> ) <sub>2</sub> titrant used (mL)
N <sub>1</sub>	=	normality of standard NaCl solution
V <sub>1</sub>	=	volume of standard NaCl solution (mL)

12.2 For determining chloride concentration:

$$\text{mg Cl/L} = \frac{(A - B) \times N \times 35,450}{\text{mL of sample}}$$

Where:

- A = titrant for sample (mL)
- B = titrant for blank (mL)
- N = normality of Hg(NO<sub>3</sub>)<sub>2</sub> titrant

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

- LCS laboratory control sample
- RPD relative percent difference
- DR data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 325.3. March 1983.
- 15.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed., SW 846. Method 9252. September 1986.

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3203

## Oil and Grease—Infrared

**Working Range:** 1.0 to 1,000 mg/L  
**Reporting Limit:** 1.0 mg/L  
**Reporting Unit:** mg/L  
**Matrix:** Water and waste

### 1.0 Scope and Application

- 1.1 The method addresses the measurement of 1,1,2-trichloro-1,2,2-trifluoroethane (fluorocarbon-113) extractable matter from surface and saline waters and industrial and domestic aqueous wastes. It is applicable to the determination of hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related matter.
- 1.2 Although the extraction procedure for the method is identical to that of gravimetric oil and grease, infrared detection permits the measurement of many relatively volatile hydrocarbons. Thus, the lighter petroleum distillates, with the exception of gasoline, may be measured with greater accuracy.

### 2.0 Method Summary

The sample is acidified to a low pH (< 2) and extracted with fluorocarbon-113. The concentration of oil and grease is determined by comparison of the infrared absorbance of the sample extract with standards.

### 3.0 Interferences

Any other substance soluble in fluorocarbon-113 will be counted as oil and grease.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling these chemicals must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Separatory Funnel, 2,000-mL with Teflon stopcock.
- 6.2 Infrared Spectrophotometer: Double-beam, scanning, capable of measuring absorbance at  $2,930\text{ cm}^{-1}$ .
- 6.3 Cells, 10-, 50-, and 100-mm path length, of infrared grade glass.
- 6.4 1,000-mL Graduated Cylinder.
- 6.5 Assorted Glassware.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the infrared spectrophotometer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Hydrochloric Acid (HCl), 6 N 1:1: Mix equal volumes of concentrated HCl and water. **Caution:** Heat-liberating reaction.
- 8.3 1,1,2-Trichloro-1,2,2-trifluoroethane: Available commercially as Fluorocarbon-113, with a boiling point of 47°C.
- 8.4 Sodium Sulfate ( $\text{Na}_2\text{SO}_4$ ): Anhydrous crystal.
- 8.5 Reference Oil: Prepare mixture, by volume, of 37.5% iso-octane, 37.5% hexadecane, and 25% chlorobenzene. Store in a sealed glass container to prevent evaporation.
- 8.6 Magnesium Sulfate ( $\text{MgSO}_4$ ): Anhydrous crystal.

## 9.0 Calibration Procedures

### 9.1 Calibration Standards

- 9.1.1 Prepare a stock solution of reference oil by rapidly transferring about 1 mL of reference solution to tared 100-mL volumetric flask. Stopper flask and weigh to nearest milligram.
- 9.1.2 Add fluorocarbon-113 and dilute to mark.
- 9.1.3 Using volumetric techniques, prepare a series of standards that covers range of interest. Normally four standards and one blank are used.
- 9.1.4 Select a pair of matched near-infrared silica cells. **Note:** Appropriate path-length cells would be 1 cm for a working range of about 4 to 40 mg; 50 mm for a range of 0.4 to 8 mg; and 100 mm for a range of 0.1 to 4 mg.
- 9.1.5 Scan standards from 3,200 to 2,700  $\text{cm}^{-1}$  with solvent in reference beam, and record results on absorbance paper. The absorbances of samples and standards are measured by constructing a straight baseline over range of scan and measuring absorbance of the peak maximum at 2,930  $\text{cm}^{-1}$  and subtracting baseline at that point. If absorbance exceeds 0.8 for a sample, select a shorter path length or dilute as required.

- 9.1.6 Prepare a calibration curve by plotting absorbance as a function of mg of reference oil.

## 10.0 Sample Preparation

- 10.1 Mark sample bottle at water meniscus for later determination of sample volume. Check pH of sample by touching inside of cap with pH paper. Add more acid if pH is not less than 2.
- 10.2 Pour sample into separatory funnel.
- 10.3 Add 30 mL of fluorocarbon-113 to sample bottle and rotate bottle to rinse sides. Transfer solvent into separatory funnel. Extract by shaking vigorously for 2 minutes. Allow layers to separate.
- 10.4 Filter solvent layer into 100-mL volumetric flask through funnel containing solvent-moistened filter paper.

**Note:** If emulsion forms that fails to dissipate, emulsion can be dispersed by pouring about 1 gram of sodium sulfate into filter paper cone and slowly draining emulsion through salt. Additional 1-gram portions can be added to cone as required.

- 10.5 Repeat extraction step twice more with additional portions (about 30 mL each) of fresh solvent, combining all solvent in volumetric flask.
- 10.6 Rinse tip of separatory funnel, filter paper, and funnel with a total of 5 to 10 mL of fluorocarbon-113 and collect rinsings in flask. Dilute extract to 100 mL with fluorocarbon-113 and stopper flask.
- 10.7 Determine volume ( $\pm 0.01$  L) of sample by refilling sample container and pouring water into graduated cylinder.

## 11.0 Sample Analysis

- 11.1 In the same manner as the standard solutions, measure the absorbance of the sample solutions. The concentration of oil and grease in the sample can be determined using the standard curve.
- 11.2 Analyze a method blank using 100 mL of fluorocarbon-113.

**12.0 Calculations**

The concentration of oil and grease in the sample is calculated as:

$$\text{mg/L total oil and grease} = \frac{R \times D}{V}$$

Where:

- R = oil and grease in solution determined from the standard curve
- D = extract dilution factor, if used
- V = sample volume (L)

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

3203

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

## 15.0 References

- 15.1 *Standard Methods for the Examination of Water and Wastewater.* 16th ed., Method 503 B. 1985.
- 15.2 *Methods for Chemical Analysis of Water and Wastes.* Method 413.2. March 1983.

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3203

## Oil and Grease (Gravimetric Only)

**Working Linear Range:** Gravimetric: infinite  
**Reporting Limit:** 5.0 to 1,000 mg/L  
**Reporting Unit:** mg/L  
**Matrix:** Water and wastes

### 1.0 Scope and Application

1.1 The method includes the measurement of 1,1,2-trichloro-1,2,2-trifluoroethane (fluorocarbon-113) extractable matter from surface and saline waters, and industrial and domestic aqueous wastes. It is applicable to the determination of relatively nonvolatile hydrocarbons, vegetable oils, animal fats, soaps, greases, and related matter.

1.2 The method is not applicable to measurement of light hydrocarbons that volatilize at temperatures below 70°C. Petroleum fuels from gasoline through No. 2 fuel oils are completely or partially lost in the solvent removal operation.

1.3 Some crude oils and heavy fuel oils contain a significant percentage of residue-type materials that are not soluble in fluorocarbon-113. Accordingly, recoveries of these materials will be low.

### 2.0 Method Summary

The sample is acidified to a low pH (< 2) and extracted with fluorocarbon-113. Oil and grease is determined by evaporating the solvent from the extract and weighing the residue.

### 3.0 Interferences

Any other substance soluble in fluorocarbon-113 will be counted as "oil and grease."

#### **4.0 Safety Precautions**

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling these chemicals must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### **6.0 Apparatus**

##### **6.1 Extraction**

6.1.1 Separatory Funnel: 2,000-mL, with Teflon stopcock.

6.1.2 Filter Paper: Whatman No. 40, 11 cm.

6.1.3 Thermometer: NIST-traceable, in 0.1°C increments.

##### **6.2 Analysis**

6.2.1 Vacuum Pump, or other source of vacuum.

6.2.2 Flask: Boiling, 125-mL (Corning No. 4100 or equivalent).

6.2.3 Distilling Head: Claisen, or equivalent.

6.2.4 Filter Paper: Whatman No. 40, 11 cm.

6.2.5 Analytical Balance: Capable of accuracy to 0.1 gram.

- 6.2.6 Snyder Column.
- 6.2.7 Water Bath: Capable of sustaining  $70^{\circ} \pm 2^{\circ}\text{C}$ .
- 6.2.8 Graduated Cylinder: 1-liter.
- 6.2.9 Assorted Glassware.
- 7.0 Routine Preventive Maintenance**
- 7.1 Perform routine preventive maintenance for the vacuum pump and water bath according to the manufacturers' directions.
- 7.2 Perform routine maintenance for balances and oven in accordance with the manufacturers' directions. Check calibration of balance daily with Class S weights. Check oven temperature daily with an NIST-traceable thermometer.
- 7.3 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.4 Examine glassware before each use for scratches and cracks, and replace as necessary.
- 8.0 Reagents and Calibration Standards**
- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Hydrochloric Acid, Concentrated HCl.
- 8.3 Hydrochloric Acid, 1:1: Mix equal volumes of concentrated HCl water.  
**Caution:** Heat-liberating reaction.
- 8.4 1,1,2-Trichloro-1,2,2-trifluoroethane: Commercially available as fluorocarbon-113. Boiling point =  $48^{\circ}\text{C}$ .
- 8.5 Sodium Sulfate: Anhydrous crystal.

3203

## 9.0 Calibration Procedures

The calibration of the balance is checked daily with Class S weights.

## 10.0 Sample Preparation

10.1 Mark sample bottle at water meniscus for later determination of sample volume. If sample was not acidified at time of collection, add acid (HCl or H<sub>2</sub>SO<sub>4</sub>) to pH < 2 to sample bottle. After mixing sample, check pH by touching pH-sensitive paper to cap to check that pH is ≤ 2. Add more acid if necessary.

10.2 Pour sample into separatory funnel.

10.3 Tare a boiling flask (predried in oven at 103°C and stored in desiccator).

10.4 Add 30 mL fluorocarbon-113 to sample bottle, and rotate bottle to rinse sides. Transfer solvent into separatory funnel. Extract by shaking vigorously for 2 minutes. Allow layers to separate, and filter solvent layer into flask through funnel containing solvent moistened filter paper.

**Note:** If an emulsion forms that fails to dissipate, it can be dispersed by pouring about 1 gram sodium sulfate into the filter paper cone and slowly draining the emulsion through the salt. Additional 1-gram portions of sodium sulfate can be added to the cone as required.

10.5 Repeat twice more with additional portions (30 mL) of fresh solvent, combining all the solvent in the boiling flask.

10.6 Rinse tip of separatory funnel, filter paper, and then funnel with 10 to 20 mL of solvent, and collect rinsings in flask.

## 11.0 Sample Analysis

11.1 Connect boiling flask to distilling head and evaporate solvent by immersing lower half of flask in water bath at 70° ± 2°C. Collect solvent for reuse. A solvent blank should accompany each set of samples.

- 11.2 When temperature in distilling head reaches  $50^{\circ} \pm 2^{\circ}\text{C}$  or flask appears dry, remove distilling head. To remove solvent vapor, sweep out flask for 15 seconds with air by inserting a glass tube connected to a vacuum source. Immediately remove flask from heat source, and wipe outside to remove excess moisture and fingerprints.
- 11.3 Cool boiling flask in desiccator for 30 minutes and weigh.
- 11.4 Determine volume of sample by refilling sample container and pouring water into graduated cylinder.

## 12.0 Calculation

$$\text{mg/L total oil and grease} = \frac{R - B}{V}$$

Where:

- R = residue, gross weight of extraction flask minus tare weight (mg)
- B = blank determination, residue of equivalent volume of extraction solvent (mg)
- V = volume of sample (L)

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement Action	Frequency	Acceptance Range	Corrective
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

LCS            laboratory control sample  
 RPD           relative percent difference  
 DR            data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPJP

**15.0 References**

- 15.1        *Standard Methods for the Examination of Water and Wastewater.* 16th ed., Method 503A. 1985.
- 15.2        *Methods for Chemical Analysis of Water and Wastes.* PB84. Method 413.1. March 1983.



## Percent Solids (Moisture)

**Working Linear Range:** 0.1 to 100%  
**Reporting Limit:** 0.1%  
**Reporting Units:** %  
**Matrix:** Sludge, soil, or sediment

### 1.0 Scope and Application

The method applies to the determination of the solids (or moisture) content in sludge, soil, or sediment samples.

### 2.0 Method Summary

An aliquot of sample is placed in a dried, preweighed evaporating dish, and the sample is weighed. The sample is then dried at 103° to 105°C and weighed, and the percentage of solids is determined.

### 3.0 Interferences

No significant interferences.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

3203

**6.0 Apparatus**

- 6.1 Evaporating Dishes: 90-mm diameter, porcelain, platinum, high silica glass.
- 6.2 Drying Oven: Capable of sustaining 103° to 105°C.
- 6.3 Analytical Balance: Capable of weighing to 0.01 gram.
- 6.4 Desiccator: Containing a desiccant with a color indicator of moisture concentration.

**7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the analytical balance and the drying oven according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Standards**

No reagents or calibration standards are prepared for the method.

**9.0 Calibration Procedure**

Check balance calibration daily with Class S weights.

**10.0 Sample Preparation**

Allow sample to come to room temperature.

**11.0 Sample Analysis**

- 11.1 Dry evaporating dish in drying oven at 103° to 105°C for at least 1 hour. Transfer dish to desiccator and allow to cool to room temperature. Note time in desiccator. Weigh dish using analytical balance. Store weighed dish in desiccator until ready for use.
- 11.2 Transfer aliquot of well mixed sample to preweighed evaporating dish. Weigh dish and sample, and record weight of sample.
- 11.3 Transfer dish and sample to drying oven, and heat for at least 1 hour at 103° to 105°C.
- 11.4 Cool dish and sample in desiccator.
- 11.5 Weigh dish and sample using analytical balance.
- 11.6 Repeat steps 11.3 through 11.5 until constant sample weight is obtained. Constant sample weight is defined as a loss in weight no greater than 0.1 gram between start weight and final weight of the last cycle.

**12.0 Calculations**

- 12.1 Calculate percent solids for sample as:

$$\% \text{ Solids} = \frac{(A - B)}{C - B} \times 100$$

Where:

- A = weight of dried solids + dish (grams)  
B = weight of dish (grams)  
C = weight of wet sample + dish (grams)

12.2 Calculate percent moisture using one of the following equations:

$$\% \text{ Moisture} = 100 - \% \text{ Solids}$$

or

$$\% \text{ Moisture} = \frac{(C - B) - (A - B)}{(C - B)} \times 100$$

Where:

- A = weight of dried solids + dish (grams)
- B = weight of dish (grams)
- C = weight of wet sample + dish (grams)

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

- Begin beginning of the analytical period
- LCS laboratory control sample

RPD relative percent difference  
DR data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

## 15.0 References

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 160.3. March 1983.
- 15.2 APHA et al. *Standard Methods for the Examination of Water and Wastewater*. 16th ed., Method 209F. 1985.

FERNALD/moisture.51



## Total Petroleum Hydrocarbons—Infrared

**Working Linear Range:** 0.2 to 1,000 mg/L  
**Reporting Limit:** Water, 0.2 mg/L  
**Reporting Units:** Water, mg/L  
**Matrix:** Water and waste

### 1.0 Scope and Application

- 1.1 The method is applicable for analysis of surface, saline, and ground waters for total recoverable hydrocarbons extracted by 1,1,2-trichloro,1,2,2-trifluoroethane (fluorocarbon-113) and analyzed by infrared spectrometry.
- 1.2 Infrared detection permits the measurement of many relatively volatile hydrocarbons, with the exception of gasoline.

### 2.0 Method Summary

The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbent. Infrared analysis of the extract is performed by direct comparison with standards.

### 3.0 Interferences

The more polar hydrocarbons, such as complex aromatic compounds and hydrocarbon derivatives of chlorine, sulfur, and nitrogen, may be adsorbed by silica gel. Any compound other than hydrocarbons and fatty matter soluble in fluorocarbon-113 and not removed by silica gel may interfere.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Separatory Funnel: 2,000 mL, with Teflon stopcock.
- 6.2 Infrared Spectrophotometer: Double-beam, scanning, capable of measuring at  $2,930\text{ cm}^{-1}$ .
- 6.3 Cells: 10-, 50-, and 100-mm path length, sodium chloride or infrared grade glass.
- 6.4 Filter Paper: Whatman No. 40, 15-cm, or equivalent.
- 6.5 Magnetic Stirrer, with Teflon-coated stirring bars.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the infrared spectrophotometer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

### 8.1 Reagents

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Hydrochloric Acid, 1:1: Mix equal volumes of concentrated HCl and water.  
**Caution:** Heat-liberating reaction.

8.1.3 1,1,2-Trichloro-1,2,2-trifluoroethane: Available commercially as fluorocarbon-113. Boiling point = 48°C.

8.1.4 Sodium Sulfate: Anhydrous crystal.

8.1.5 Silica Gel: 60-200 mesh, Davidson Grade 950 or equivalent. Should contain 1 to 2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.

8.1.6 Magnesium Sulfate ( $\text{MgSO}_4$ ): Anhydrous crystal.

8.2 Reference Oil Calibration Mixtures: Pipet 15.0 mL n-hexadecane, 15.0 mL isooctane, and 10 mL chlorobenzene into a 50-mL glass stoppered bottle. Maintain integrity of mixture by keeping stoppered except when withdrawing aliquots.

## 9.0 Calibration Procedure

### 9.1 Calibration Standards

9.1.1 Prepare stock solution of reference oil by rapidly transferring about 1 mL of reference solution to tared 100-mL volumetric flask. Stopper flask and weigh to nearest milligram.

9.1.2 Add fluorocarbon-113 and dilute to mark.

9.1.3 Using volumetric techniques, pipet appropriate volumes from stock (step 9.1.1) and dilute to 100 mL with fluorocarbon-113 (according to path length of cell to be used). Four standards plus a blank are required.

- 9.1.4 Select a pair of matched near-infrared silica cells. **Note:** Appropriate path-length cells would be 1 cm for a working range of about 4 to 40 mg, 50 mm for a range of 0.4 to 8 mg, and 100 mm for a range of 0.1 to 4 mg.
- 9.1.5 Scan standards from 3,200 to 2,700  $\text{cm}^{-1}$  with solvent in reference beam, and record results on absorbance paper. Absorbances of samples and standards are measured by constructing a straight baseline over range of scan and measuring absorbance of the peak maximum at 2,930  $\text{cm}^{-1}$  and subtracting baseline at that point. If absorbance exceeds 0.8 for sample, select a shorter path-length or dilute as required.
- 9.1.6 Prepare calibration curve by plotting absorbance as function of mg reference oil.

## 10.0 Sample Preparation

- 10.1 Mark sample bottle at water meniscus for later determination of sample volume. Check sample pH by touching inside of cap with pH paper. Add more hydrochloric acid if pH is not less than 2.
- 10.2 Pour sample into separatory funnel.
- 10.3 Add 30 mL fluorocarbon-113 to sample bottle and rotate bottle to rinse sides. Transfer solvent to separatory funnel.
- 10.4 Extract by shaking vigorously for 2 minutes. Allow layers to separate.
- 10.5 Filter solvent layer into 100-mL volumetric flask through funnel containing solvent-moistened filter paper.

**Note:** If an emulsion forms that fails to dissipate, it can be dispersed by pouring 1 gram of sodium sulfate into filter paper cone and slowly draining emulsion through the salt. Additional 1-gram portions can be added to cone as required.

- 10.6 Repeat extraction step twice more with 30-mL portions of fresh solvent. Combine solvent in volumetric flask.
- 10.7 Rinse tip of separatory funnel, filter paper, and funnel with 5 to 10 mL of solvent, and collect rinsings in flask.

- 10.8 Dilute extract to 100 mL with fluorocarbon-113. If extract is known to contain more than 100 mg of nonhydrocarbon organic material, pipet appropriate portion of sample into 100-mL volumetric flask and dilute to volume.
- 10.9 Discard about 5 to 10 mL solution from the volumetric flask.
- 10.10 Add 3 grams of silica gel and stirring bar. Stopper volumetric flask and stir solution for at least 5 minutes with magnetic stirrer.
- 11.0 Sample Analysis**
- 11.1 After silica gel has settled in sample extract, fill clean cell with solution and determine absorbance. If absorbance exceeds absorbance of highest standard, an appropriate dilution must be made. If the absorbance exceeds 0.8, dilute and reanalyze.
- 11.2 The possibility that the absorptive capacity of the silica gel has been exceeded can be tested by adding another 3 grams silica gel to the extract and repeating the treatment and determination.
- 11.3 Determine concentration of petroleum hydrocarbons in the extract by comparing response against calibration curve.
- 12.0 Calculations**
- 12.1  $\text{mg/L petroleum hydrocarbons} = \frac{R \times D}{V}$

Where:

- R = petroleum hydrocarbons, determined from calibration plot (mg)
- D = extract dilution factor
- V = volume of sample, determined by refilling sample bottle to calibration line and correcting for acid addition if necessary (L)

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPJP

### 15.0 Reference

- 15.1 *Methods for Chemical Analysis of Water and Wastes*. PB84-128677, Method 418.1. March 1983.
- 15.2 *Standard Method for the Examination of Water and Wastewater*. 17th ed., Method 5520F and G. 1989.



## Total Dissolved Solids

**Working Linear Range:** 10 to 20,000 mg/L  
**Reporting Limits:** 10 mg/L  
**Reporting Unit:** mg/L  
**Matrix:** Water

### 1.0 Scope and Application

The method measures filterable residue (total dissolved solids) in a water matrix. Filterable residue is defined as solids capable of passing through a glass fiber filter and dried to constant weight at 180°C.

### 2.0 Method Summary

A well-mixed sample is filtered through a standard glass fiber filter. The filtrate is evaporated and dried to constant weight at 180°C.

### 3.0 Interferences

- 3.1 Highly mineralized waters containing significant concentrations of calcium, magnesium, chloride, or sulfate may be hygroscopic and will require prolonged drying, desiccation, and rapid weighing.
- 3.2 Samples containing high concentrations of bicarbonate will require careful and possibly prolonged drying at 180°C to insure that all the bicarbonate is converted to carbonate.
- 3.3 If the sample contains a high level of dissolved solids, then too much residue may form upon evaporation causing the residue to crust over and entrap water. Total residue should be limited to 200 mg. This can be minimized by using a smaller volume of sample.

### 4.0 Safety Precautions

The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples

determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Glass fiber Filter Disks: 9.0-cm, without organic binder, such as Whatman type 934-AH, Gelman type A/E, or equivalent.
- 6.2 Filter Holder: Membrane filter funnel or Gooch crucible adapter.
- 6.3 Suction Flask: 500-mL.
- 6.4 Evaporating Dishes: 100-mL volume, porcelain (Vycor or platinum dishes may be substituted).
- 6.5 Drying Oven: Capable of sustaining  $180^{\circ} \pm 2^{\circ}\text{C}$ .
- 6.6 Desiccator.
- 6.7 Analytical Balance: Capable of weighing to 0.1 mg.
- 6.8 Thermometer: Capable of measuring temperature  $\pm 0.2^{\circ}\text{C}$  and traceable to an NIST thermometer.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the analytical balance and drying oven according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

All references to water assume the use of ASTM Type II water.

## 9.0 Calibration Procedures

Check balance calibration before each weighing session with NIST-approved Class S weights. Check oven temperature with an NIST-traceable thermometer.

## 10.0 Sample Preparation

Allow sample to warm to room temperature.

## 11.0 Sample Analysis

### 11.1 Preparation of Glass Filter

11.1.1 Place filter on membrane filter apparatus with wrinkled side up, or insert into bottom of suitable Gooch crucible.

11.1.2 While vacuum is applied, wash filter with three successive 20-mL volumes of ASTM Type II water.

11.1.3 Remove all traces of water by continuing to apply vacuum after water has passed through. Discard all washing.

### 11.2 Preparation of Evaporating Dish

11.2.1 Heat clean evaporating dish to  $180^{\circ} \pm 2^{\circ}\text{C}$  for at least 1 hour.

11.2.2 Remove dish from oven and transfer to a desiccator. Cool to room temperature and weigh to the nearest 0.1 mg immediately before use. Record initial weight of evaporation dish.

### 11.3 Analytical Procedure

11.3.1 Assemble filtering apparatus and begin suction.

- 11.3.2 Shake sample vigorously and rapidly transfer 50 mL to funnel using 50-mL graduated cylinder. If total filterable residue is low, a larger volume may be filtered. Note: Choose sample volume to yield between 2.5 and 200 mg residue.
- 11.3.3 Rinse nonfilterable residue and filter walls with three volumes (about 10 mL each) of water, allowing complete drainage between each washing. Remove all traces of water by continuing to apply vacuum for 3 minutes after filtration is complete.
- 11.3.4 Transfer filtrate to weighed evaporating dish, and evaporate to dryness in drying oven.
- 11.3.5 Dry evaporated sample for at least 1 hour at  $180^{\circ} \pm 2^{\circ}\text{C}$ . Cool in desiccator, and weigh to the nearest 0.1 mg.
- 11.3.6 Repeat drying cycle until constant weight is obtained or until weight loss is less than 0.5 mg.

## 12.0 Calculations

Calculate filterable residue (TDS) as:

$$\text{TDS (mg/L)} = \frac{(A - B) \times 1000}{C}$$

Where:

- A = weight of dried residue + dish (mg)  
B = weight of dish (mg)  
C = volume of sample used (mL)

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

3203

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80-120%	Qualify data
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0-20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 Reference**

U.S. EPA. *Methods for Chemical Analysis of Water and Waste*. PB84-128677. Method 160.1. March 1983.

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3203

## Phosphorus Analysis—Single Reagent Method

**Working Linear Range:** 0.01 to 0.5 mg/L  
**Reporting Limit:** 0.05 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water

### 1.0 Scope and Application

- 1.1 The method covers the determination of total phosphorus, orthophosphate, and total organic phosphorus in surface and ground waters. Phosphorus occurs in natural waters and in wastewaters almost solely as phosphates. These are classified as orthophosphates ( $\text{PO}_4$ ), acid-hydrolyzable phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates. Phosphates occur in solutions, in particles or detritus, or in the bodies of aquatic organisms.
- 1.2 Many forms of phosphorus can be quantified using analytical techniques; however, the method is concerned only with the measurement of total phosphorus, orthophosphate, and total organic phosphorus.
- 1.2.1 Total phosphorus is all phosphorus present in the sample, regardless of form, and will be measured using the persulfate digestion procedure.
- 1.2.2 Total orthophosphate is a measure of all the inorganic phosphorus [ $(\text{PO}_4)^{-3}$ ] and is determined directly through colorimetry without digestion.
- 1.2.3 Total organic phosphorus is the inorganic and oxidizable organic phosphorus in the sample. It is calculated as total phosphorus minus hydrolyzable phosphorus and orthophosphate rather than measured directly. Hydrolyzable phosphorus must be determined to measure total organic phosphorus and is the phosphorus in the sample measured by the sulfuric acid hydrolysis procedure.

### 2.0 Method Summary

- 2.1 Phosphorus analyses usually consist of two steps:

- Conversion of the phosphorus form of interest to dissolved orthophosphate through hydrolysis or digestion
- Colorimetric determination of dissolved orthophosphate

2.2 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. Color intensity is proportional to the phosphorus concentration.

### 3.0 Interferences

- 3.1 Arsenates react with the molybdate reagent to produce a blue color similar to that formed with phosphate. Concentrations as low as 0.1 mg arsenic per liter of solution may interfere with the phosphate determination.
- 3.2 High iron concentrations can cause precipitation of and subsequent loss of phosphorus.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

**6.0 Apparatus**

- 6.1 Spectrophotometer: Suitable for measurements at 650 or 880 nm with a light path 1 cm or longer.
- 6.2 Acid-washed Glassware: All glassware should be washed with hot 1:1 HCl and rinsed with water. Glassware should not be used for anything but phosphorus determination. Glassware must never be washed with commercial detergent because it often contains phosphates.
- 6.3 Laboratory Hot Plate.
- 6.4 pH Meter.

**7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the spectrophotometer and the pH meter according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Solutions**

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ) Solution, 5 N: Dilute 70 mL of concentrated sulfuric acid with water to 500 mL. **Caution:** Heat-liberating reaction.
- 8.3 Antimony Potassium Tartrate Solution ( $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ ): Weigh 1.3715 grams  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot \frac{1}{2}\text{H}_2\text{O}$ , dissolve in 400 mL water in a 500-mL volumetric flask, and dilute to volume. Store at  $4^\circ \pm 2^\circ\text{C}$  in a dark, glass-stoppered bottle.
- 8.4 Ammonium Molybdate Solution ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ): A stock solution is available commercially. It can be prepared by dissolving 20 grams

$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  in 500 mL of water. Store in a plastic bottle at  $4^\circ \pm 2^\circ\text{C}$ .

- 8.5 Ascorbic Acid, 0.1 M. Dissolve 1.76 grams of ascorbic acid in 100 mL of water. The solution is stable for at least 1 week if stored at  $4^\circ \pm 2^\circ\text{C}$ .
- 8.6 Combined Reagent: Mix the above reagents in the following proportions for 100 mL of the mixed reagent: 50 mL of 5 N sulfuric acid, 5 mL of the antimony potassium tartrate solution, 15 mL of ammonium molybdate solution, and 30 mL of ascorbic acid solution. Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand a few minutes until turbidity disappears before proceeding. Since the stability of the solution is limited, it must be prepared fresh for each run.
- 8.7 Sulfuric Acid Solution, 11 N. Slowly add 310 mL concentrated sulfuric acid to 600 mL water. **Caution:** Heat-liberating reaction. When cool, dilute to 1 liter.
- 8.8 Ammonium Persulfate: Prepare a solution so that 5 mL contains 0.4 gram. Place 4 grams of ammonium persulfate in a 50-mL volumetric flask. Add approximately 25 mL of water and swirl flask until ammonium persulfate is dissolved. Dilute solution to 50 mL. 5 mL = 0.4 gram.
- 8.9 Stock Phosphorus Solution: Dry potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) in a  $105^\circ\text{C}$  oven for at least 1 hour. After cooling in a desiccator, dissolve in water 0.2197 gram of  $\text{KH}_2\text{PO}_4$ . Dilute the solution to 1 liter. 1.0 mL = 0.05 mg P.
- 8.10 Sodium Hydroxide, 1 N. Dissolve 40 grams NaOH in 600 mL water. Cool and dilute to 1 liter.
- 9.0 Calibration Procedure**
- 9.1 Preparation of Standard Phosphorus Solutions
- 9.1.1 Dilute 10.0 mL of stock phosphorus solution to 1 liter with water; 1.0 mL =  $0.5 \mu\text{g}$  P. Using the standard solution, prepare the following standards in 50.0-mL volumetric flasks:

Standard Phosphorus Solution (mL)	Concentration (mg/L)
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

9.1.2 It is not necessary to prepare all the standards; four points and one blank can be used to define a straight line. It is necessary, however, that enough standards be prepared so as to bracket all the samples.

## 9.2 Calibrating the Spectrophotometer

9.2.1 Prepare the standard calibration solutions in the same manner as samples as outlined in Section 11.

9.2.2 Prepare a calibration blank consisting of ASTM Type II water in the same manner as the samples.

9.2.3 Measure the absorbance of the standard solutions and the calibration blank. Prepare a calibration curve by plotting absorbance as a function of concentration.

## 10.0 Sample Preparation

If sample has been refrigerated, allow it to warm to room temperature.

## 11.0 Sample Analysis

**Note:** For highly colored or turbid samples, a sample blank may be analyzed that consists of a sample to which all reagents are added except ascorbic acid and antimonyl potassium tartrate. The sample blank value is subtracted from the absorbance of each sample. Samples that fall above the concentration of the highest calibration standard are diluted and reanalyzed.

3203

## 11.1 Total Phosphorus

- 11.1.1 If the sample has been refrigerated, allow it to warm to room temperature.
- 11.1.2 Pipette 50 mL of sample into a 125-mL Erlenmeyer flask.
- 11.1.3 Add 5 mL of ammonium persulfate solution to flask.
- 11.1.4 Place Erlenmeyer flask on preheated hot plate and boil sample gently for 30 to 40 minutes or until a final volume of about 10 mL is reached. Do not allow sample to go dry.
- 11.1.5 Remove sample from hot plate and allow it to cool to room temperature. Measure pH with pH meter, and adjust sample pH to  $7.0 \pm 0.2$  by slowly adding 1 N NaOH. The pH of the solution can also be monitored using phenolphthalein as an indicator. If the sample is not clear at this point, add 2 to 3 drops of 1 N sulfuric acid solution and filter. Dilute sample to 50 mL in volumetric flask.
- 11.1.6 Add 8.0 mL of combined reagent to sample and mix thoroughly. After at least 10 minutes but no longer than 30 minutes, measure the color absorbance of each sample at 650 or 880 nm with the spectrophotometer using the reagent blank as the reference solution.
- 11.1.7 Measure and note the absorbance of the sample.

## 11.2 Orthophosphate

- 11.2.1 Pipette 50.0 mL of sample into a clean, dry 125-mL Erlenmeyer flask. Check sample pH. If necessary, adjust pH to  $7.0 \pm 0.2$  with 1 N NaOH using pH meter. If the sample is not clear at this point, add 2 to 3 drops of the 1 N sulfuric acid solution and filter.
- 11.2.2 Add 8.0 mL of combined reagent to sample and mix thoroughly. After at least 10 minutes but no longer than 30 minutes, measure color absorbance of each sample at 650 or 880 nm with the spectrophotometer using the reagent blank as the reference solution.
- 11.2.3 Measure and note absorbance of sample.

### 11.3 Total Hydrolyzable Phosphorus

11.3.1 Total hydrolyzable phosphorus is measured by the sulfuric acid hydrolysis procedure, and minus predetermined orthophosphates. Outlined below is the process for determining hydrolyzable phosphorus; total organic phosphorus is calculated in Section 12.0.

11.3.2 Pipette 50 mL of sample into a clean, dry Erlenmeyer flask. Add 1 mL of 11 N sulfuric acid solution.

11.3.3 Boil gently on preheated hot plate for 30 to 40 minutes or until a final volume of about 10 mL is reached. Do not allow sample to go to dryness.

11.3.4 Remove sample from hot plate and allow it to cool to room temperature. Dilute sample to about 30 mL with distilled water. Check sample pH. If necessary, adjust pH to  $7.0 \pm 0.2$  with 1 N NaOH using pH meter. If sample is not clear at this point, add 2 to 3 drops of 1 N sulfuric acid solution and filter. Dilute sample to 50 mL using volumetric flask.

11.3.5 Add 8.0 mL of combined reagent to sample and mix thoroughly. After at least 10 minutes but no longer than 30 minutes, measure color absorbance of each sample at 650 or 880 nm with the spectrophotometer using the reagent blank as the reference solution.

11.3.6 Measure and note absorbance of sample.

### 12.0 Calculations

A standard calibration curve is prepared by plotting the absorbance values of the standards as a function of the concentration of phosphorus in the standards. Both total phosphorus and orthophosphate can be obtained by using the standard curve and the experimental absorbance. However, total organic phosphorus must be calculated using the formula:

$$\text{TOP} = \text{TP} - (\text{OP} + \text{HP})$$

Where:

TOP = total organic phosphorus  
TP = total phosphorus  
OP = orthophosphate  
HP = hydrolyzable phosphorus

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

- Begin beginning of the analytical period
- ICVS initial calibration verification sample
- CCVS continuing calibration verification sample
- LCS laboratory control sample
- RPD relative percent difference
- DR data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA. *Methods for the Chemical Analysis of Water and Wastes*. PB84-128677. Method 365.2.
- 15.2 *Standard Methods for Examination of Water and Wastes*. 17th ed., Method 4500-P E. 1989.



## Surfactants (MBAS)

**Working Linear Range:** Can be diluted for infinite range  
**Reporting Limit:** 0.02 mg/L calculated as LAS  
**Reporting Units:** mg/L  
**Matrix:** Water

### 1.0 Scope and Application

The method is applicable to the measurement of all species of methylene blue active substances (MBAS) in surface, ground, and drinking waters. It cannot be used to measure specific species, and it is nonapplicable to saline waters.

### 2.0 Method Summary

The dye methylene blue in aqueous solutions reacts with anionic-type surface active materials to form a blue colored salt. The salt is extractable with chloroform, and the intensity of color produced is proportional to the concentration of MBAS.

### 3.0 Interferences

Chlorides at concentrations of 1,000 mg/L show a positive interference, and so the method is not applicable to brine samples.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Chloroform is toxic and should be used under a fume hood. The analyst must wear safety glasses and gloves when working with this solvent. Chloroform should not be inhaled. Do not allow chloroform to come in contact with skin or eyes.

3203

## **5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## **6.0 Apparatus**

6.1 Separatory Funnels: 500-mL, preferably with inert TFE stopcocks and stoppers.

6.2 Glass Funnels.

6.3 Glass Wool.

6.4 Pipets.

6.5 UV/visible Spectrometer: For use at 652 nm with a light path of 1 cm or longer.

6.6 Taylor Tubes.

## **7.0 Routine Preventive Maintenance**

7.1 Perform routine preventive maintenance for the spectrophotometer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## **8.0 Reagents and Calibration Standards**

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Phenolphthalein Indicator: Alcoholic, available commercially.

8.3 Sodium Hydroxide (NaOH), 1.0 N.

152

3203

- 8.4 Sulfuric Acid ( $\text{H}_2\text{SO}_4$ ), 1.0 and 6.0 N.
- 8.5 Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ), 30%.
- 8.6 Stock LAS Calibration Solution: LAS (linear alkylbenzene sulfonate) is the most widely used anionic surfactant and is available commercially. It may comprise any or all of 26 isomers.
- 8.6.1 Weigh 0.1645 gram of LAS reference material (EPA-certified). If other reference materials are used, weigh an amount to produce a solution such that 1 mL = 1 mg LAS. Dilute to 100 mL with water. Store in refrigerator. Prepare weekly.
- 8.7 Standard LAS solution: Dilute 1.0 mL stock LAS solution to 100 mL with water. This standard must be prepared daily.
- 8.8 Stock Methylene Blue Reagent: Weigh 300 mg methylene blue. Dilute to 1,000 mL with water.
- 8.9 Working Methylene Blue Reagent: Dilute 100 mL stock solution to 1,000 mL with water.
- 8.10 Wash Solution
- 8.10.1 Combine 500 mL of water, 6 to 8 mL concentrated  $\text{H}_2\text{SO}_4$ , and 50 grams  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . **Caution:** Heat-liberating reaction. Dilute to 1 liter with water.
- 8.11 Calibration Standard: Prepare at least four calibration standards by diluting an aliquot of the standard to 400 mL with water.

Aliquot (mL)	Final Concentration (mg/L)
0.0	0.0
0.8	0.02
2.0	0.05
5.0	0.125
25.0	0.625
50.0	1.250
100.0	2.500

**9.0 Calibration Procedure**

- 9.1 Prepare calibration standards as described in step 8.7.
- 9.2 Prepare a calibration blank using water.
- 9.3 Extract and measure the absorbance of each standard solution using the process detailed in Section 11.

**10.0 Sample Preparation**

Allow sample to equilibrate to ambient temperature for accurate volumetric measurements.

**11.0 Sample Analysis**

- 11.1 Add 400 mL of sample to 500-mL separatory funnel.
- 11.2 Add 5 to 10 drops phenolphthalein indicator and adjust pH of solution by adding 1 N NaOH (solution will turn pink).
- 11.3 Add H<sub>2</sub>SO<sub>4</sub> dropwise until solution is colorless.
- 11.4 Add 10 mL chloroform and 25 mL methylene blue reagent.
  - 11.4.1 Shake 30 seconds. Allow phases to separate, swirl, and let settle.
  - 11.4.2 Drain chloroform into 125-mL separatory funnel.

**Note:** If blue color of aqueous phase becomes faint or disappears, discard sample and repeat total process with a smaller sample aliquot.
- 11.5 Repeat chloroform extraction three times. Combine extracts for a total of 40 mL plus rinsate from funnel tip into 125-mL separatory funnel.
- 11.6 Add 50 mL wash solution to separatory funnel.
- 11.7 Shake 30 seconds. Allow phases to separate, swirl, and let settle.
- 11.8 Drain chloroform layer into 100-mL Taylor tubes through glass wool.

- 11.9 Extract wash solution twice with 10 mL of chloroform. Add chloroform to Taylor tubes.
- 11.10 Rinse glass wool with chloroform, add to extracts, and dilute to 100 mL with chloroform.
- 11.11 Measure absorbance of standards and samples against blank of chloroform at 652 nm, according to the manufacturer's direction.

## 12.0 Calculation

- 12.1 Prepare a calibration curve by plotting absorbance of standards as a function of concentration in mg/L. Determine sample concentration by comparing sample absorbance with standard curve.
- 12.2 Report as MBAS, calculated as linear alkylbenzene sulfonate, using the equation

$$\text{mg MBAS} = \frac{\mu\text{g apparent LAS}}{\text{mL original sample}}$$

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

3203

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

### 15.0 Reference

*Standard Methods for Examination of Water and Wastes.* 17th ed., Method 5540C. 1989.

FERNALD/surfact.51



**Phenolics, Total Recoverable  
(Colorimetric, Automated 4-AAP with Distillation)**

3203

**Working Linear Range:** 0.002 to 0.500 mg/L  
**Reporting Limit:** 0.002 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and waste

**1.0 Scope and Application**

- 1.1 The method is applicable to the analysis of drinking, ground, surface, and saline waters and domestic and industrial aqueous waste.
- 1.2 The method is capable of measuring phenolic materials from 2 to 500  $\mu\text{g/L}$  in the aqueous phase using phenol as a standard. The working ranges are 2 to 200  $\mu\text{g/L}$  and 10 to 500  $\mu\text{g/L}$ , depending on the autoanalyzer instrument manifold used.

**2.0 Method Summary**

This automated method is based on the distillation of phenol and subsequent reaction of the distillate with alkaline ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) and 4-amino-antipyrine (4-AAP) to form a red complex that is measured at 505 or 520 nm.

**3.0 Interferences**

- 3.1 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of  $< 4.0$  with  $\text{H}_2\text{SO}_4$  and aerating briefly by stirring.
- 3.2 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of an excess of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be biased low.
- 3.3 Background contamination from plastic tubing and sample containers can be eliminated by filling the wash receptacle by siphon (using Kel-F tubing) and using glass tubes for samples and standards.

3203

**4.0 Safety Precautions**

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling them must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

**5.0 Sample Collection and Handling**

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

**6.0 Apparatus**

- 6.1 Technicon Autoanalyzer (I or II), or equivalent.
- 6.1.1 Sampler: Equipped with continuous mixer.
- 6.1.2 Manifold.
- 6.1.3 Proportioning Pump II or III.
- 6.1.4 Heating Bath with distillation coil.
- 6.1.5 Distillation Head.
- 6.1.6 Colorimeter equipped with a 50-mm flowcell and 505- or 520-nm filter.
- 6.1.7 Recorder.

3203

**7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the autoanalyzer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Standards**

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Distillation Reagent: Slowly add 100 mL of concentrated phosphoric acid (85%  $H_3PO_4$ ) to 800 mL of water, cool, and dilute to 1 liter. **Caution:** Heat-liberating reaction.
- 8.3 Buffered Potassium Ferricyanide: Dissolve 2.0 grams potassium ferricyanide, 3.1 grams boric acid, and 3.75 grams potassium chloride in 800 mL of water. Adjust pH to 10.3 with 1 N sodium hydroxide and dilute to 1 liter. Add 0.5 mL of Brij-35. Prepare fresh weekly.
- 8.4 Sodium Hydroxide, NaOH (1 N): Dissolve 40 grams NaOH in 500 mL of water, cool, and dilute to 1 liter.
- 8.5 4-Aminoantipyrine: Dissolve 0.65 gram of 4-aminoantipyrine in 800 mL of water and dilute to 1 liter. Prepare fresh daily.
- 8.6 Ferrous Ammonium Sulfate: Dissolve 1.1 grams ferrous ammonium sulfate in 500 mL water containing 1 mL  $H_2SO_4$ , and dilute to 1 liter with freshly boiled and cooled water.
- 8.7 Stock Phenol: Dissolve 1.0 gram phenol in 500 mL of water and dilute to 1,000 mL. Add 0.5 mL concentrated  $H_2SO_4$  as preservative (1.0 mL = 1.0 mg phenol). **Caution:** This solution is toxic.
- 8.8 Standard Phenol Solution A: Dilute 10.0 mL of stock phenol solution to 1,000 mL with water (1.0 mL = 0.01 mg phenol).

- 8.9 Standard Phenol Solution B: Dilute 100.0 mL of standard phenol Solution A to 1,000 mL with water (1.0 mL = 0.001 mg phenol).
- 8.10 Standard Phenol Solution C: Dilute 100.0 mL of standard phenol Solution B to 1,000 mL with water (1.0 mL = 0.0001 mg phenol).
- 8.11 Using standard Solutions A, B, or C, prepare one group of the following standards in 100-mL volumetric flasks. Each standard should be preserved by adding 2 drops of concentrated H<sub>2</sub>SO<sub>4</sub> to 100.0 mL:

Standard Solution (mL)	Concentration (µg/L)
<b>Solution C</b>	
1.0	1.0
2.0	2.0
3.0	3.0
5.0	5.0
<b>Solution B</b>	
1.0	10.0
2.0	20.0
5.0	50.0
10.0	100.0
<b>Solution A</b>	
2.0	200.0
3.0	300.0
5.0	500.0

## 9.0 Calibration Procedures

- 9.1 Measure the absorbance of the four calibration standards and one blank.
- 9.2 Prepare a standard calibration curve by plotting absorbance as a function of concentration.
- 9.3 Immediately after preparing the curve, analyze an initial calibration verification sample (ICVS) to verify the calibration. The acceptance criteria for the ICVS is 90 to 110% recovery.

## 10.0 Sample Preparation

Add concentrated  $H_2SO_4$  to 100 mL of sample for a final sample pH of  $< 2$ .

## 11.0 Sample Analysis

- 11.1 Set up the manifold according to manufacturer's directions.
- 11.2 Fill wash receptacle by siphon. Use Kel-F tubing with a fast flow (1 L/hr).
- 11.3 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding water through sample line. Use polyethylene tubing for sample line. **Note:** If new tubing is used, a 2-hour warmup time is needed for a stable baseline.
- 11.4 Place phenol calibration standards in sampler in order of decreasing concentration. Complete loading of sampler tray with QC samples and unknown samples using glass tubes.
- 11.5 Switch sample from water to sampler line and begin analysis.

## 12.0 Calculations

Prepare a standard calibration curve by plotting absorbance as a function of concentration. Determine the concentration of phenolic compounds in the sample by measuring the absorbance of the solution and determining the concentration from the standard curve.

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

- Begin beginning of the analytical period
- ICVS initial calibration verification sample
- CCVS continuing calibration verification sample
- LCS laboratory control sample
- RPD relative percent difference
- DR data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPJP

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 420.2. March 1983.
- 15.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. SW 846, Method 9066. 3rd ed. November 1986, with Final Update I.



3203

## Phenolics, Total Recoverable (Spectrophotometric, Manual 4-AAP with Distillation)

**Working Linear Range:** 1.0 to 250.0  $\mu\text{g/L}$   
**Reporting Limit:** 5  $\mu\text{g/L}$   
**Reporting Units:**  $\mu\text{g/L}$   
**Matrix:** Water and waste

### 1.0 Scope and Application

- 1.1 The method is applicable to the analysis of ground, drinking, surface, and saline waters and domestic and industrial aqueous waste.
- 1.2 The method is capable of measuring phenolic materials at the 5- $\mu\text{g/L}$  level when the colored end product is extracted and concentrated in a solvent phase using phenol as a standard. It is also capable of measuring phenolic materials that contain more than 50  $\mu\text{g/L}$  in the aqueous phase (without solvent extraction) using phenol as a standard.
- 1.3 It is not possible to use the method to differentiate between different kinds of phenols.

### 2.0 Method Summary

Phenolic materials react with 4-aminoantipyrine in the presence of potassium ferricyanide at a pH of 10 to form a stable, reddish-brown antipyrine dye. The amount of color produced is a function of the concentration of phenolic material.

### 3.0 Interferences

- 3.1 For most samples a preliminary distillation is required to remove interfering materials.
- 3.2 Color response of phenolic materials with 4-aminoantipyrine is not the same for all compounds. Because phenolic-type wastes usually contain a variety of phenols, it is not possible to use a mixture of substituted phenols as a standard. For this reason, phenol has been selected as a standard and any color produced by the reaction of other phenolic compounds is reported as

3203

phenol. The value will represent the minimum concentration of phenolic compounds present in the sample.

- 3.3 Interferences from sulfur compounds are eliminated by acidifying the sample to a pH of  $< 4$  with  $H_2SO_4$  and aerating at the sample briefly by stirring.
- 3.4 Oxidizing agents such as chlorine, detected by the liberation of iodine upon acidification in the presence of potassium iodide, are removed immediately after sampling by the addition of ferrous ammonium sulfate. If chlorine is not removed, the phenolic compounds may be partially oxidized and the results may be biased low.

#### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

#### 6.0 Apparatus

- 6.1 Distillation Apparatus: All glass, consisting of a 1-liter Pyrex distilling apparatus with Graham condenser.
- 6.2 pH Meter.
- 6.3 Spectrophotometer: Double-beam with a light path of at least 1 cm for use at 460 or 510 nm.

3203

- 6.4 Funnels.
- 6.5 Filter Paper.
- 6.6 Membrane Filters.
- 6.7 Separatory Funnels: 500 or 1,000 mL.
- 6.8 Nessler Tubes: Short or long form.
- 6.9 Volumetric Flasks: Class A.
  
- 7.0 Routine Preventive Maintenance**
- 7.1 Perform routine preventive maintenance for the spectrophotometer the pH meter according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.
  
- 8.0 Reagents and Calibration Standards**
- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Sulfuric Acid Solution ( $H_2SO_4$ ): Concentrated.
- 8.3 Buffer Solution: Dissolve 16.9 grams  $NH_4Cl$  in 143 mL concentrated  $NH_4OH$ , and dilute to 250 mL with water. 2 mL of buffer should adjust 100 mL of distillate to pH 10.
- 8.4 Aminoantipyrine Solution: Dissolve 2 grams of 4-aminoantipyrine in water and dilute to 100 mL.
- 8.5 Potassium Ferricyanide Solution: Dissolve 8 grams of  $K_3Fe(CN)_6$  in water and dilute to 100 mL.

165

3203

- 8.6 Stock Phenol Solution: Boil rapidly approximately 1,200 mL of water and then cool to room temperature. Transfer 500 mL of the water to a 1-liter volumetric flask. Add 1 gram phenol and swirl to mix. Dilute to mark with boiled water. 1.0 mL = 1.0 mg phenol. Note: Solution is hygroscopic and toxic.
- 8.7 Working Solution A: Dilute 10 mL stock phenol solution to 1 liter with water. 1 mL = 10  $\mu$ g phenol.
- 8.8 Working Solution B: Dilute 100 mL of working solution A to 1,000 mL with water. 1 mL = 1  $\mu$ g phenol.
- 8.9 Chloroform.
- 8.10 Ferrous Ammonium Sulfate: Boil rapidly approximately 1,200 mL of water that has 1 mL concentrated sulfuric acid and then cool to room temperature. Transfer 500 mL of water to a 1-liter volumetric flask. Add 1.1 grams of ferrous ammonium sulfate and swirl to mix. Dilute to mark with boiled water.

## 9.0 Calibration Procedures

- 9.1 Direct photometric method for concentrations of phenolics greater than 50  $\mu$ g/L.
- 9.1.1 Using working Solution A, prepare the following standards in 100-mL volumetric flasks:

Working Solution A (mL)	Concentration ( $\mu$ g/L)
(Calibration blank)	0.0
0.0	50.0
0.5	100.0
1.0	200.0
2.0	500.0
5.0	800.0
8.0	1000.0
10.0	

- 9.1.2 It is not necessary to prepare all the standards; four points and one blank can be used to define a straight line. However, it is necessary that enough

standards be prepared so as to bracket all the samples. Calibration standards must be processed the same as samples.

- 9.1.3 The absorbance of each standard is measured and then a calibration curve is prepared by plotting absorbance as a function of concentration at 510 nm.
- 9.2 Chloroform extraction method for concentrations of phenolics greater than 1  $\mu\text{g/L}$ . **Caution:** The method should be performed in a fume hood since chloroform is toxic.
- 9.2.1 Using working Solution B (step 8.8), prepare the following standards in 100-mL volumetric flasks.

Working Solution B (mL)	Concentration ( $\mu\text{g/L}$ )
0.0	0.0
3.0	6.0
5.0	10.0
10.0	20.0
20.0	40.0
25.0	50.0

- 9.2.2 It is not necessary to prepare all the standards; four points and one blank can be used to define a straight line. However it is necessary that enough standards be prepared so as to bracket all the samples.
- 9.2.3 Follow procedure as outlined in step 11.2.
- 9.2.4 The absorbance of each standard is measured at 460 nm and then a calibration curve is prepared by plotting absorbance as a function of concentration.
- 10.0 Sample Preparation**
- 10.1 Distillation
- 10.1.1 Transfer 500 mL of sample into a beaker. Adjust sample pH to 4 with concentrated  $\text{H}_2\text{SO}_4$  (1 mL/L). Transfer sample to distillation apparatus.
- 10.1.2 Begin distilling the sample. When 450 mL of sample has distilled over to receiving flask, stop distillation, and add 50 mL of warm water to the

distillation flask. Resume distillation and stop distilling when 500 mL of sample have been collected in receiving flask.

10.1.3 If the distillate is turbid, filter through a prewashed membrane filter.

10.2 If direct photometric method is to be used, proceed to step 11.1.

10.3 If chloroform extraction method is to be used, proceed to step 11.2.

## 11.0 Sample Analysis

### 11.1 Direct Photometric Method

11.1.1 To 100 mL of distillate (or to an aliquot diluted to 100 mL), add 2 mL of buffer solution and swirl to mix. Sample pH should be  $10 \pm 0.2$ .

11.1.2 Add 2.0 mL aminoantipyrine solution and mix.

11.1.3 Add 2.0 mL potassium ferricyanide solution and mix.

11.1.4 Allow color to develop for 15 minutes, and measure absorbance at 510 nm.

### 11.2 Chloroform Extraction Method

11.2.1 Transfer 500 mL of distillate (or an aliquot diluted to 500 mL) to separatory funnel. Sample should not contain more than 50  $\mu\text{g}$  phenol.

11.2.2 Add 10 mL of buffer solution to the sample and mix. The pH should be  $10 \pm 0.2$ .

11.2.3 Add 3.0 mL aminoantipyrine solution and mix.

11.2.4 Add 3.0 mL potassium ferricyanide solution and mix.

11.2.5 After 3 minutes, add 25 mL of chloroform. Shake separatory funnel at least 10 times, let chloroform settle, shake again 10 times, and allow layers to separate.

11.2.6 Filter chloroform extract through filter paper. Do not add more chloroform.

11.2.7 Measure absorbance of sample at 460 nm.

3203

**12.0 Calculations**

A standard calibration curve is prepared by plotting absorbance as a function of concentration. The concentration of phenolic compounds in the sample is determined by measuring the absorbance of the solution and determining the concentration in the sample from the appropriate standard curve.

**13.0 Data Package Deliverables**

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

**14.0 Quality Control (QC) Requirements**

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90-110%	Recalibrate
CCVS	1/15	90-110%	Recalibrate
LCS	Begin	80-120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75-125%	Qualify data
Duplicate Sample	1/20	0-20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

3203

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 420.1. March 1983.
- 15.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed., SW 846, Method 9065. November 1986, with Final Update I.

FERNALD/phen-spe.51



## Sulfate (Colorimetric, Automated, Methylthymol Blue)

**Working Linear Range:** 1 to 300 mg/L  
**Reporting Limit:** 1.0 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and waste

### 1.0 Scope and Application

This automated method is applicable to drinking, surface, and ground waters and domestic and industrial aqueous waste.

### 2.0 Method Summary

Barium sulfate is formed by the reaction of the  $\text{SO}_4^{-2}$  with barium chloride ( $\text{BaCl}_2$ ) at a low pH. At high pH excess barium reacts with methylthymol blue to produce a blue chelate. Uncomplexed methylthymol blue is gray. The amount of gray uncomplexed methylthymol blue indicates the concentration of sulfate.

### 3.0 Interferences

- 3.1 An ion-exchange column is used to eliminate interferences from multivalent cations.
- 3.2 Turbid samples should be filtered or centrifuged to remove turbidity.
- 3.3 Samples with pH below 2 should be neutralized because high acid concentrations elute cations from the ion-exchange resin.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

### 6.1 Automated Continuous-flow Analytical Instrument

#### 6.1.1 Sampler.

#### 6.1.2 Manifold: High- or low-level.

#### 6.1.3 Proportioning Pump.

#### 6.1.4 Heating Bath operable at specified temperature.

#### 6.1.5 Colorimeter equipped with 15-mm flowcell and 460-nm interference filters.

#### 6.1.6 Filters of specified transmittance.

#### 6.1.7 Recorder.

### 6.2 Ion Exchange Column

#### 6.2.1 Glass Tubing: 7.5 inches long by 2.0 mm I.D. and 3.6 mm O.D.

#### 6.2.2 Pipet.

#### 6.2.3 Glass Wool.

## 7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the continuous-flow instrument according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Barium Chloride: Dissolve 1.526 grams of barium chloride dihydrate ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in 500 mL of water and dilute to 1 liter.

8.3 Methylthymol Blue: Dissolve 0.1182 gram of methylthymol blue (3'3'-bis-N, N-bis carboxymethyl-amino methylthymolsulfone-phthalein pentasodium salt) in 25 mL of barium chloride solution. Add 4 mL of 1.0 N hydrochloric acid, which changes the color to bright orange. Add 71 mL of water and dilute to 500 mL with ethanol. The pH of the solution is 2.6. The reagent should be prepared the day before analysis and stored in a brown polyethylene bottle in the refrigerator.

8.4 Buffer, pH  $10.5 \pm 0.5$ : Dissolve 6.75 grams of ammonium chloride in 500 mL of water. Add 57 mL of concentrated ammonium hydroxide and dilute to 1 liter with water. **Caution:** Heat-liberating reaction.

8.5 Buffered EDTA: Dissolve 40 grams of tetrasodium EDTA in pH 10.5 buffer and dilute to 1 liter with buffer.

8.6 Sodium Hydroxide Solution (50%) 12.5 N: Dissolve 500 grams NaOH in 600 mL of water, cool, and dilute to 1 liter.

8.7 Sodium Hydroxide, 0.18 N: Dilute 14.4 mL of sodium hydroxide solution to 1 liter.

- 8.8 Ion-exchange Resin: Bio-Rex 70, 20-50 mesh, sodium form, Bio-Rad Laboratories, Richmond, California. Free from fines by stirring with several portions of water and decant the supernate before settling is complete.
- 8.9 Dilution Water: Add 0.75 mL of sulfate stock solution and 3 drops of Brij-35 (available from Technicon) to 2 liters of water.
- 8.10 Sulfate Stock Solution, 1 mL = 1 mg  $\text{SO}_4^{-2}$ : Dissolve 1.479 grams of  $\text{Na}_2\text{SO}_4$  (dried to a constant weight at 105°C) in water and dilute to 1 liter.
- 8.11 Dilute Sulfate Solution, 1 mL = 0.1 mg  $\text{SO}_4^{-2}$ : Dilute 100 mL of sulfate stock solution to 1 liter.
- 8.12 High-level Working Standards, 10 to 300 mg/L: Prepare high-level working standards by diluting the following volumes of stock standard to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
1	10
5	50
10	100
15	150
25	250
30	300

- 8.13 Low-level Working Standards, 0.5 to 30 mg/L: Prepare low-level working standards by diluting the following volumes of dilute sulfate solution to 100 mL:

Stock Solution (mL)	Concentration (mg/L)
0.5	0.5
1	1.0
5	5.0
10	10.0
15	15.0
25	25.0
30	30.0

3203

## 9.0 Calibration Procedure

It is not necessary to prepare all the standard solutions; four points that bracket the expected sample concentration range and one blank are sufficient. The absorbance of each solution is measured using the procedure detailed in Section 11. Once the absorbance of each solution has been measured, a standard calibration curve is prepared by plotting peak heights as a function of concentration.

### 10.0 Sample Preparation

- 10.1 Allow sample to come to room temperature.
- 10.2 Turbid samples should be filtered or centrifuged.

### 11.0 Sample Analysis

- 11.1 Set up autoanalyzer according to manufacturer's directions for either high or low concentrations.
- 11.2 The ion-exchange column is prepared by pulling a slurry of the resin into a piece of glass tubing 7.5-inch long, 2.0-mm I.D., and 3.6-mm O.D. This can be done using a pipet and a loose-fitting glass wool plug in the tubing. Care should be taken to avoid allowing air bubbles into the column. If air bubbles become trapped, the column should be prepared again. The column can exchange the equivalent of 35 mg of calcium. For the high-level manifold, this corresponds to about 900 samples with 200 mg/L Ca. The column should be prepared as often as necessary to ensure that no more than 50% of its capacity is used.
- 11.3 Allow colorimeter, recorder, and printer to warm up for 30 minutes. Pump all reagents until a stable baseline is achieved.
- 11.4 Place sulfate standards (in duplicate) in order of decreasing concentration of sulfate in the sampler. Fill up the tray with the QCS and samples. Since the chemistry is nonlinear, the 150-mg/L standard is set at 50% on the recorder using the standard calibration control on the colorimeter.
- 11.5 Switch sample line to sampler and start analysis.
- 11.6 At the end of each day, wash the system with the buffered EDTA solution. This is done by placing the methylthymol blue line and the sodium hydroxide

line in water for a few minutes and then in the buffered EDTA solution for 10 minutes. Wash system with water for 15 minutes before shutting down.

## 12.0 Calculations

Prepare a standard calibration curve by plotting absorbance as a function of concentration. The concentration of sulfate in the sample is determined by measuring the peak heights of the solution and determining the concentration in the sample from the standard curve. The control standards must be analyzed every hour to ensure that the system remains properly calibrated. Because the chemistry is nonlinear, the 150-mg/L standard is set at 50% on the recorder using the standard calibration control on the colorimeter.

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	every hour	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference

DR data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

3203

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 375.2. March 1983.
- 15.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed., SW 846, Method 9036. November 1986, with Final Update I.

FERNALD/sulf-mb.51



## Sulfate (Turbidimetric)

**Working Linear Range:** 1.0 to 40.0 mg/L  
**Reporting Limit:** 1.0 mg/L  
**Reporting Units:** mg/L  
**Matrix:** Water and wastes

### 1.0 Scope and Application

The method is applicable to drinking, surface, and ground waters and domestic and industrial aqueous wastes. It is suitable for all concentration ranges of sulfate ( $\text{SO}_4^{-2}$ ); however, to obtain reliable readings, use a sample aliquot containing not more than 40 mg/L of  $\text{SO}_4^{-2}$ .

### 2.0 Method Summary

Sulfate ion is converted to a barium sulfate suspension under controlled conditions. The resulting turbidity is determined by a nephelometer, filter photometer, or spectrophotometer and compared with a curve prepared from standard sulfate solution.

### 3.0 Interferences

- 3.1 Color and turbidity due to the sample matrix can cause positive interferences that must be accounted for by use of blanks.
- 3.2 Silica in concentrations over 500 mg/L will interfere.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling them must be practiced. Personal protective equipment must

include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Magnetic Stirrer: Variable speed so that it can be held constant just below splashing. Use identical shapes and sizes of magnetic stirring bars.
- 6.2 Photometer (one of the following, given in order of preference).
  - 6.2.1 Nephelometer.
  - 6.2.2 Spectrophotometer: For use at 420 nm with light path of 4 to 5 cm.
  - 6.2.3 Filter Photometer: With a violet filter having a maximum near 420 nm and a light path of 4 to 5 cm.
- 6.3 Stopwatch: If magnetic stirrer is not equipped with an accurate timer.
- 6.4 Measuring Spoon: Capacity 0.2 to 0.3 mL.
- 6.5 pH Meter.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the photometric device according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

**8.0 Reagents and Calibration Standards**

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Conditioning Reagent: Slowly add 30 mL concentrated HCl to 300 mL water, 100 mL 95% ethanol or isopropanol, and 75 grams NaCl in solution in a container. **Caution:** Heat-liberating reaction. Add 50 mL glycerol and mix.

8.3 Barium Chloride ( $\text{BaCl}_2$ ): Crystals, 20 to 30 mesh.

8.4 Sodium Carbonate Solution, approximately 0.05 N: Dry 3 to 5 grams primary standard  $\text{Na}_2\text{CO}_3$  at  $250^\circ\text{C}$  for 4 hours and cool in desiccator. Weigh  $2.5 \pm 0.2$  grams (to the nearest mg), transfer to 1-liter volumetric flask, and fill to mark with water.

8.5 Proprietary Reagents: Hach Sulfaver, or equivalent.

8.6 Standard Sulfate Solution ( $1.00 \text{ mL} = 100 \mu\text{g SO}_4^{-2}$ )

8.6.1 Standard Sulfate Solution from  $\text{H}_2\text{SO}_4$

8.6.1.1 Standard Sulfuric Acid, 0.1 N: Dilute 3.0 mL concentrated  $\text{H}_2\text{SO}_4$  to 1 liter with water. **Caution:** Heat-liberating reaction. Standardize against 40.0 mL of 0.05 N  $\text{Na}_2\text{CO}_3$  solution with about 60 mL water by titrating potentiometrically to a pH of about 5. Lift electrodes and rinse into beaker. Boil gently for 3 to 5 minutes under a watch glass cover. Cool to room temperature. Rinse cover glass into beaker. Continue titration to pH inflection point. Calculate normality of  $\text{H}_2\text{SO}_4$  as:

$$N = \frac{A \times B}{53.00 \times C}$$

Where:

A =  $\text{Na}_2\text{CO}_3$  weighed into 1-liter flask (grams)  
B =  $\text{Na}_2\text{CO}_3$  solution used in standardization (mL)  
C = acid used in titration (mL)

- 8.6.1.2 Standard Acid, 0.02 N: Dilute appropriate amount of 0.1 N standard acid to 1 liter (use 200 mL standard acid if normality is 0.1000 N). Check by standardization against 15 mL of 0.05 N  $\text{Na}_2\text{CO}_3$  solution.
- 8.6.1.3 Place 10 mL 0.02 N standard sulfuric acid in a 100-mL volumetric flask and dilute to mark.
- 8.6.2 Standard Sulfate Solution from  $\text{Na}_2\text{SO}_4$ : Dissolve 147.9 mg anhydrous  $\text{Na}_2\text{SO}_4$  in water in 1-liter volumetric flask, and swirl to mix. Dilute to mark with water.

## 9.0 Calibration Procedure

It is not necessary to prepare all the standard solutions; four points and one blank are sufficient. Space standards at 5 mg/L increments in the 0- to 40-mg/L sulfate range. The absorbance of each solution is measured using the procedure detailed in Section 11. Once the absorbance of each solution has been measured, a standard calibration curve is prepared by plotting absorbance as a function of concentration. Above 50 mg/L the accuracies decrease and the suspensions lose stability. Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of the calibration curve.

## 10.0 Sample Preparation

Allow sample to warm to room temperature.

## 11.0 Sample Analysis

### 11.1 Formation of Barium Sulfate Turbidity

- 11.1.1 Place 100-mL sample or a suitable portion diluted to 100 mL into 250-mL Erlenmeyer flask.
- 11.1.2 With a pipet, add 5 mL conditioning reagent.
- 11.1.3 Gently add stirring bar to flask and begin stirring solution.
- 11.1.4 While solution is being stirred, add a measured spoonful of  $\text{BaCl}_2$  crystals and begin timing immediately.

3203

- 11.1.5 Stir for  $60 \pm 2$  seconds at constant speed.
- 11.2 Measurement of Barium Sulfate Turbidity
  - 11.2.1 Immediately after stirring period has ended, pour solution into absorbance cell.
  - 11.2.2 Measure turbidity at 30-second intervals for 4 minutes.
  - 11.2.3 Record maximum reading obtained in the 4-minute period.
- 11.3 Correction for Sample Color and Turbidity: Analyze a method blank using steps 11.1 and 11.2 without addition of barium chloride.

## 12.0 Calculation

- 12.1 Determine mg/L  $\text{SO}_4^{-2}$  from standard curve.
- 12.2 Correct for blank using the equation:

$$\text{mg/L SO}_4^{-2} = \text{mg/L SO}_4^{-2} \text{ for sample} - \text{mg/L SO}_4^{-2} \text{ for blank}$$

- 12.3  $\text{mg/L SO}_4^{-2} = \frac{\text{mg SO}_4^{-2} \times 1,000}{\text{mL sample}}$

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20 or every hour	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

**Where:**

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 U.S. EPA. *Methods for Chemical Analysis of Water and Wastes*. PB84-128677. Method 375.4. March 1983.
- 16.2 U.S. EPA. *Test Methods for Evaluating of Solid Waste*. 3rd ed., SW 846, Method 9038. November 1986, with Final Update I.

FERNALD/sulf-tur.51



## Fluoride

**Working Linear Range:** 0.1 to 1.4 mg/L F<sup>-</sup>  
**Reporting Limit:** 0.1 mg/L F<sup>-</sup>  
**Reporting Units:** mg/L F<sup>-</sup>  
**Matrix:** Water and wastes

### 1.0 Scope and Application

The method is applicable to the measurement of fluoride in ground, drinking, surface, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

The SPADNS colorimetric method is based on the reaction between fluoride and a zirconium-dye lake. Fluoride reacts with the dye lake, dissociating a portion of it into a colorless complex anion (ZrF<sub>6</sub><sup>2-</sup>) and the dye. As the amount of fluoride increases, the color produced becomes progressively lighter.

### 3.0 Interferences

- 3.1 The addition of the highly colored SPADNS reagent must be done accurately because the fluoride concentration is measured as a difference of absorbance in the blank and the sample. A small error in reagent addition is the most prominent source of error in this test.
- 3.2 Care must be taken to avoid overheating the flask above the level of the solution by maintaining an even flame entirely under the boiling flask.
- 3.3 The colorimetric method is susceptible to interfering substances of various degrees. Table 1 lists common interferents. Because they are neither linear in effect nor algebraically additive, mathematical compensation is impossible. Whenever any one substance is present in sufficient quantity to produce an error of 0.1 mg/L or whenever the total interfering effect is in doubt, the sample must be distilled.

**Table 1**  
**Concentration of Some Substances Causing 0.1-mg/L**  
**Error at 1.0 mg F/L in Fluoride Method**

(SPADNS)		
Substance	Conc. (mg/L)	Type of Error
Alkalinity (CaCO <sub>3</sub> )	5000	-
Aluminum (Al <sup>3+</sup> )	0.1*	-
Chloride (Cl <sup>-</sup> )	7000	+
Chlorine	-	Remove completely with arsenite
Color and turbidity	-	Remove or compensate for
Iron	10	-
Hexametaphosphate ([NaPO <sub>3</sub> ] <sub>6</sub> )	1	+
Phosphate (PO <sub>4</sub> <sup>3-</sup> )	16	+
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	200	-

\* On immediate reading. Tolerance increases with time: after 2 hours, 3.0; after 4 hours, 30.

#### 4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

6.1 Distillation Apparatus: 1-liter, round-bottom, long-neck borosilicate glass boiling flask, connecting tube, an efficient condenser, a thermometer adapter, and a thermometer reading to 200°C. All connections should be ground glass. Available commercially.

6.2 Colorimeter (one of the following)

6.2.1 Spectrophotometer for use at 570 nm providing a light path of at least 1 cm.

6.2.2 Filter photometer equipped with greenish yellow filter having maximum transmittance at 550 to 580 nm and light path of at least 1 cm.

6.3 Soft Glass Beads.

6.4 Magnetic Stirrer with Teflon-coated stirring bar.

6.5 Class A Volumetric Flasks.

## 7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the colorimeter according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>): Concentrated, reagent grade.

- 8.2 Silver Sulfate ( $\text{Ag}_2\text{SO}_4$ ): Crystals, reagent grade.
- 8.3 Water: All references to water assume the use of ASTM Type II water.
- 8.4 Stock Fluoride Solution: Available commercially. To prepare, dissolve 0.221 gram anhydrous sodium fluoride ( $\text{NaF}$ ) in water in 1-liter volumetric flask. Dilute to mark with water. 1.00 mL = 0.1 mg fluoride.
- 8.5 Standard Fluoride Solution: Place 100 mL stock fluoride solution in a 1-liter volumetric flask. Dilute to mark with water. 1.0 mL = 0.010 mg fluoride.
- 8.6 SPADNS Solution: Dissolve 0.958 gram of SPADNS (sodium 2-(parasulfo-phenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate, in water in 500-mL volumetric flask. Dilute to mark. Solution is stable for at least 1 year if protected from light.
- 8.7 Zirconyl-acid Reagent: Dissolve 0.133 gram zirconyl chloride octahydrate ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) in approximately 25 mL water in a 500-mL volumetric flask. Add 350 mL concentrated HCl and dilute to mark with water.  
**Caution:** Heat-liberating reaction.
- 8.8 Zirconyl-acid-SPADNS Reagent: Mix equal volumes of SPADNS solution and zirconyl-acid reagent. The combined reagent is stable for at least 2 years if protected from light.
- 8.9 Reference Solution: Add 10 mL SPADNS solution to 100 mL water. Dilute 7 mL concentrated HCl to 10 mL and add to the dilute SPADNS solution. The solution is used for zeroing the colorimeter. Solution is stable for at least 1 year if protected from light.
- 8.10 Sodium Arsenite Solution: Dissolve 5.0 grams  $\text{NaAsO}_2$  in water in a 1-liter volumetric flask and dilute to the mark with water. **Caution:** Solution is toxic because of the presence of arsenic salt. Avoid skin contact, inhalation, or ingestion.

## 9.0 Calibration Procedure

Prepare calibration solution by diluting the following volumes of the working standard fluoride solution (step 8.5) to 100 mL with water:

Standard Solution (mL)	Concentration (mg/L)
1.0	0.1
2.0	0.2
4.0	0.4
5.0	0.5
7.0	0.7
8.0	0.8
10.0	1.0
12.0	1.2
14.0	1.4

It is not necessary to prepare all the standard solutions; four points and one blank are sufficient. The absorbance of 50 mL of each solution is measured using the procedure detailed in Section 11. Once the absorbance of each solution is measured, a standard calibration curve is prepared by plotting absorbance as a function of concentration.

## 10.0 Sample Preparation

### 10.1 Preliminary Distillation

10.1.1 Place 400 mL water in distilling flask.

10.1.2 Carefully add 200 mL concentrated  $\text{H}_2\text{SO}_4$  and swirl until contents are homogeneous. **Caution:** Heat-liberating reaction.

10.1.3 Add 25 to 35 glass beads, and connect apparatus making sure all joints are tight.

10.1.4 Heat slowly at first, then as rapidly as the efficiency of the condenser will permit (distillate must be cool) until temperature of flask contents reaches exactly  $180^\circ\text{C}$ . Discard distillate. This process removes fluoride contamination and adjusts the acid-water ratio for subsequent distillation.

### 10.2 Sample Distillation

10.2.1 Cool contents of flask to  $120^\circ\text{C}$  or below.

10.2.2 Add 300 mL of sample, mix thoroughly, and distill until temperature reaches  $178^\circ\text{C}$  to prevent sulfate carryover. Do not heat above  $178^\circ \pm 1^\circ\text{C}$ .

- 10.2.3 Add  $\text{Ag}_2\text{SO}_4$  at a ratio of 5 mg/mg  $\text{Cl}^-$  when chloride samples are distilled.
- 10.2.4 Use sulfuric acid solution in flask repeatedly until contaminants from samples accumulate to the extent that recovery is affected or interferences appear in the distillate. Check periodically by distilling standard fluoride samples.
- 10.2.5 High fluoride samples may require that the still be flushed by using water and combining distillates.

### 11.0 Sample Analysis

- 11.1 Use a 50-mL sample or a portion diluted to 50 mL. Adjust temperature of sample to that used for standard curve.
- 11.2 Pipet 5.0 mL each of SPADNS solution and zirconyl-acid reagent or 10.0 mL of mixed acid-zirconyl-SPADNS reagent to each sample and mix well.
- 11.3 Set photometer to zero with reference solution and immediately obtain absorbance readings of samples.

### 12.0 Calculation

- 12.1 Prepare a standard calibration curve by plotting absorbance as a function of concentration. The concentration of fluoride compounds in the sample is determined by measuring the absorbance of the solution and determining the concentration in the sample from the standard curve.

- 12.2 Calculate as

$$\text{mg F}^-/\text{L} = \frac{\text{mg F}^- \times 1,000}{\text{mL of Sample}}$$

12.3 When the solution requires dilution:

$$\text{mg F}^{-}/\text{L} = \frac{A}{\text{mL sample}} \times \frac{B}{C}$$

Where:

A = mass of F<sup>-</sup> determined from plotted curve (mg)

The ratio B/C applies only when a sample is diluted to a volume B, and a portion C is taken from it for color development.

12.4 When the prepared 0 mg F<sup>-</sup>/L standard is used to set the photometer, alternatively calculate fluoride concentration as follows:

$$\text{mg F}^{-}/\text{L} = \frac{A_0 - A_x}{A_0 - A_1}$$

Where:

A<sub>0</sub> = absorbance of the prepared 0 mg F<sup>-</sup>/L standard  
A<sub>1</sub> = absorbance of a prepared 1 mg F<sup>-</sup>/L standard  
A<sub>x</sub> = absorbance of the prepared sample

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

#### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

#### 15.0 References

- 15.1 *Methods for Chemical Analysis of Water and Wastes*. PB84-128677, Method 340.1. March 1983.
- 15.2 *Standard Methods for the Examination of Water and Wastewater*. 17th ed., Method 4500-FD. 1989.



## Total Organic Halides

**Working Linear Range:** 5.0 to 1,000  $\mu\text{g/L}$

**Reporting Limit:** 5.0  $\mu\text{g/L}$

**Reporting Units:**  $\mu\text{g/L}$

**Matrix:** Water

### 1.0 Scope and Application

1.1 The method is applicable to the measurement of total organic halides in ground, drinking, surface, and saline waters.

1.2 The presence of halogenated organic molecules is thought to be indicative of synthetic chemical contamination. There is no target compound list for this method; rather, the result is the sum of halogenated compounds present in the sample. Examples of halogenated compounds that contribute to the TOX result include:

- Trihalomethanes
- Organic solvents such as trichloroethylene and other halogenated alkanes and alkenes
- Chlorinated and brominated pesticides and herbicides
- Chlorinated aromatics such as hexachlorobenzene
- Polychlorinated biphenyls (PCBs)
- High molecular weight, partially chlorinated aquatic humic substances

1.3 The method measures only the total molar amount of dissolved organically bound halogen retained on the carbon adsorbent; it does not measure the molar amount of organically bound halogens on undissolved solids. The method yields no information about the structure or nature of the organic compounds to which the halogens are bound or about the individual halogens present. It is sensitive to organically bound chloride, bromide, and iodide but does not detect fluorinated organics.

3203

## 2.0 Method Summary

2.1 The method comprises four major steps.

2.1.1 Dissolved organic material is separated from inorganic halides and concentrated from aqueous solution by adsorption onto activated carbon.

2.1.2 Inorganic halides present on the activated carbon are removed by competitive displacement by nitrate ions.

2.1.3 The activated carbon with adsorbed organic material is introduced into a furnace that pyrolyzes organic carbon to carbon dioxide and the bound halogens to hydrogen halides (HX).

2.1.4 The HX is transported in a carrier gas stream to a micro-coulometric titration cell where the amount of halide is quantified by measuring the current produced by silver-ion precipitation of the halides.

2.2 As mentioned above, there is no specific target analyte as this is a qualitative measure of dissolved halogenated organic material. The practical range of the determination is 5.0 to 1,000  $\mu\text{g/L}$ .

## 3.0 Interferences

3.1 The method is applicable only to aqueous samples free of particulate matter because suspended solids may prevent the sample from passing through the column. Interference can be minimized by removing suspended solids through settling or centrifuging and then decanting the supernatant, but agitating the sample must be minimized to avoid loss of volatile compounds.

3.2 Granular activated carbon is used to concentrate organic material from the sample, and it may be a major source of variability in the analysis as well as the method detection limit. Ideally, activated carbon should:

- Have a low halide content, preferably less than 1,000 ng Cl<sup>-</sup>/40 mg carbon
- Readily release adsorbed inorganic halides on nitrate washing
- Be homogeneous

193

- Readily adsorb all organic halide compounds even in the presence of large excesses of other organic material

3.3 Because activated carbon plays an integral role in the analytical method, each batch of carbon is tested before samples are analyzed. Additionally, because proper quantification may also be affected by the adsorptive capacity of the carbon, the method includes serial adsorptions of each sample portion.

3.4 Inorganic substances such as chloride, chlorite, chlorate, bromide, and iodide also adsorb on activated carbon. Therefore, sample results may be biased high if inorganic halides are not removed. Interference can be minimized by flushing the column with nitrate ion, which causes competitive desorption from the activated carbon of inorganic halide species, hence washing inorganic halides from the system. This works, however, only with samples in which the inorganic halide concentration is about 20,000 times the organic halide concentration or less, or the chloride concentration is less than 500 mg Cl/L sample. For samples with inorganic halide concentrations greater than 20,000 times the organic halide concentration, the results of the method may be invalid.

#### 4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

- 6.1 Adsorption System: Available commercially (see Figure 1).
- 6.2 Granulated Activated Carbon (GAC): Available commercially (e.g., Filtrasorb-400, or equivalent). GAC must be ground or milled and screened to a 100/200 mesh range. The apparent halide background should be 1,000 ng Cl<sup>-</sup> or less upon combustion of 40 mg of GAC.
- 6.3 Cerafelt: Available commercially from Johns-Manville, or equivalent. The material is used to plug the adsorption module and to hold 40 mg of GAC in the adsorption column. **Caution:** Do not touch this material with your fingers. Any residue will contaminate the carbon.
- 6.4 Analytical System: Available commercially. The system (see Figure 2) consists of a titration system, boat sampler, pyrolysis furnace, micro-coulometer with integrator and a titration cell, and either a strip chart recorder or a data management system.
- 6.5 Adsorption Columns: Pyrex, 5 cm long, 6-mm O.D., 2-mm I.D.

## 7.0 Routine Preventive Maintenance

- 7.1 Perform routine preventive maintenance for the TOX analyzer according to the manufacturer's directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.
- 7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

- 8.1 Water: All references to water assume the use of ASTM Type II water.
- 8.2 Sodium Sulfite (Na<sub>2</sub>SO<sub>3</sub>) 0.1 M: Dissolve 12.6 grams ACS reagent grade sodium sulfite in 500 mL of water, and swirl to mix. Dilute to 1 liter.
- 8.3 Concentrated Nitric Acid (HNO<sub>3</sub>): Available commercially.

3203

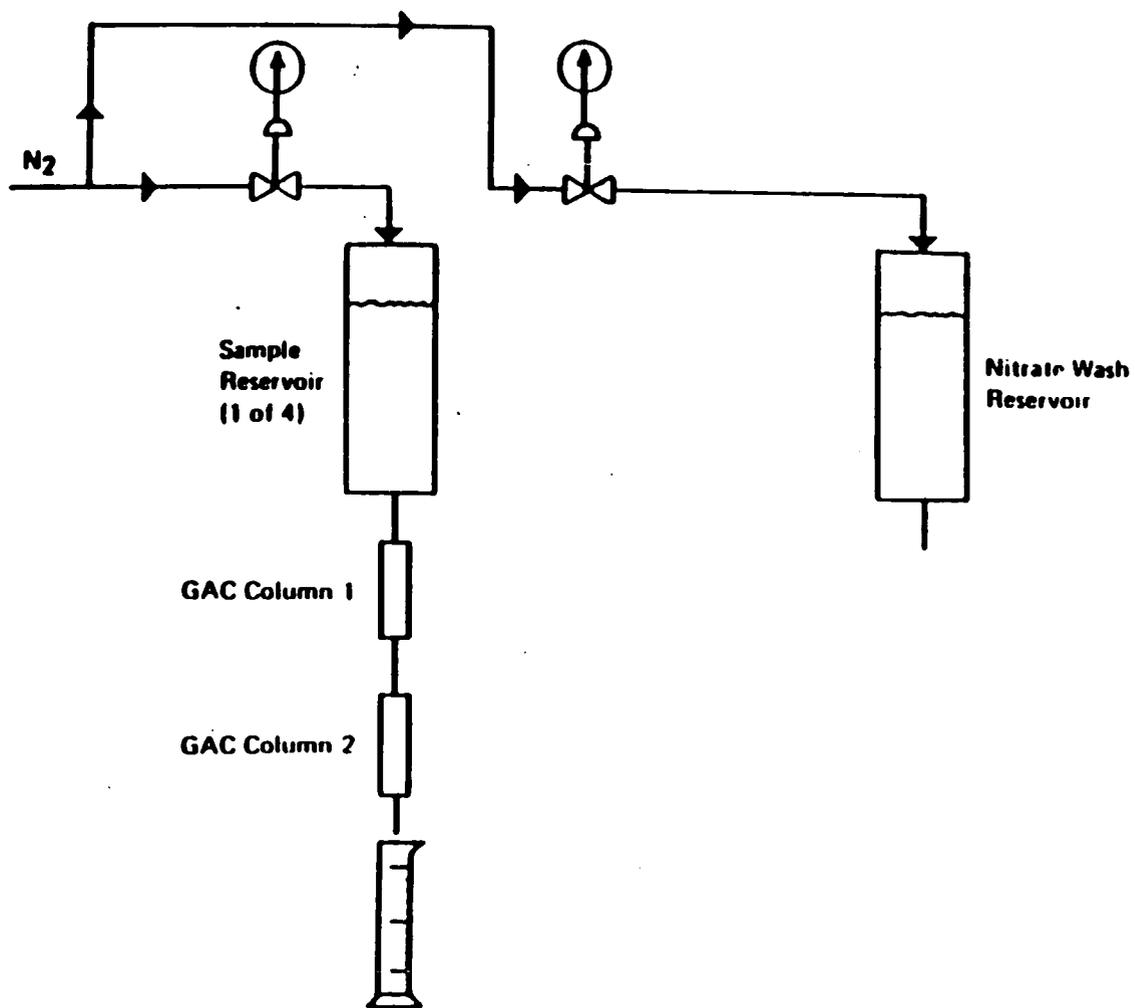


Figure 1. Schematic diagram of adsorption system.

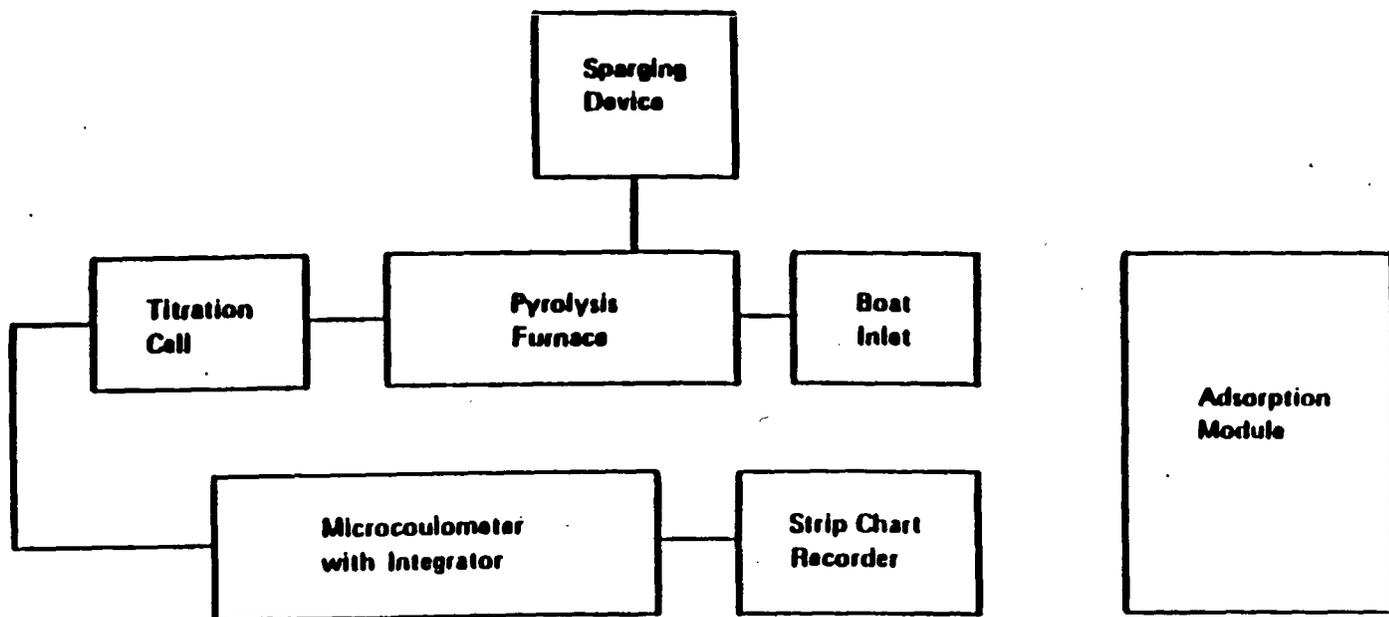


Figure 2. Flowchart of analytical system.

- 8.4 Nitrate-wash Solution: 5,000 mg  $\text{NO}_3^-/\text{L}$ . Dissolve 8.2 grams of potassium nitrate ( $\text{KNO}_3$ ) in 500 mL of water. Dilute to 1 liter.
- 8.5 Carbon Dioxide ( $\text{CO}_2$ ): Gas, 99.9% purity.
- 8.6 Oxygen ( $\text{O}_2$ ): Gas, 99.9% purity.
- 8.7 Nitrogen ( $\text{N}_2$ ): Prepurified.
- 8.8 Acetic Acid Solution, 70%: Dilute 7 volumes of glacial acetic acid with 3 volumes of water. **Caution:** Heat-liberating reaction.
- 8.9 Stock Trichlorophenol Solution: Prepare stock solution by weighing accurately 1.856 grams of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.  $1 \mu\text{L} = 10 \mu\text{g Cl}^-$ .
- 8.10 Calibration Trichlorophenol Solution: Dilute 5 mL of trichlorophenol stock solution to 100 mL with methanol.  $1 \mu\text{L} = 500 \text{ ng Cl}^-$ .
- 8.11 Adsorption Efficiency Trichlorophenol Standard: Dilute  $10 \mu\text{L}$  of stock solution into 1 liter of water.  $100 \mu\text{g Cl}^-/\text{liter}$ .
- 9.0 Calibration Procedure**
- 9.1 This section summarizes the steps necessary for calibrating the instrument. The exact details are provided in the manufacturer's directions.
- 9.2 The instrument is calibrated using two points: the nitrate-wash method blank and one calibration point.
- 9.2.1 Nitrate-wash Method Blank: Using the sample analysis procedure presented in Section 11, analyze replicate samples of the nitrate-wash solution to establish the instrument baseline. A nitrate-wash method blank should be analyzed after every ten field samples.
- 9.2.2 Instrument Calibration: Using the sample analysis procedure presented in Section 11, rinse the column with nitrate-wash solution and then inject the column with  $10 \mu\text{L}$  of the instrument calibration solution.  $1 \mu\text{L} = 500 \text{ ng Cl}^-$ ; therefore,  $10 \mu\text{L} = 5.0 \mu\text{g/L Cl}^-$ .

## 10.0 Sample Preparation

10.1 Special care should be practiced to minimize loss of volatile compounds. Samples should not be opened until immediately before analysis. Residual chlorine in the water sample in the form of  $\text{Cl}_2$  or  $\text{ClO}_2$  first must be reduced to chloride and the sample acidified before it may be processed through the GAC.

10.1.1 To 0.5 liter of sample add 1 mL of 0.1 M of sodium sulfite solution prepared as outlined under step 8.2.

10.1.2 To the same sample, add about 1 mL of reagent grade nitric acid ( $\text{HNO}_3$ ) to acidify the sample to about pH 2.

## 11.0 Sample Analysis

11.1 This section summarizes the analytical sequence. The exact details are provided in the manufacturer's directions.

### 11.2 Adsorption

11.2.1 Check the adsorption efficiency of each newly prepared batch of carbon by analyzing 100 mL of adsorption efficiency standard. The net recovery should be within 5% of the standard value; if it is not, discard the carbon.

11.2.2 Prepare and then connect two columns in series, each containing 40 mg of 100/200 mesh activated carbon.

11.2.3 Pour 100 mL of sample into the sample reservoir, and allow the sample to pass through the activated-carbon columns at a rate of about 3 mL/min.

**Note:** The volume of sample depends on the concentration of TOX in the sample. For concentrations of TOX greater than 500  $\mu\text{g}$  TOX/L, dilute the sample so that 100 mL contains about 1 to 50  $\mu\text{g}$  TOX.

11.2.4 Wash columns (still plumbed in series) with 2 mL of nitrate solution to displace inorganic chloride ions. Decrease flow rate of nitrate solution to approximately 2 mL/min.

- 11.2.5 If columns are not analyzed immediately, plug the ends, place in a VOA vial and store in a cool, dark place until analysis begins. Be sure that label identifies upper and lower columns.
- 11.3 Pyrolysis
- 11.3.1 Pyrolysis is a two-step process. First the volatile compounds are pyrolyzed in a CO<sub>2</sub>-rich atmosphere at a low temperature (200°C) to ensure conversion of brominated trihalomethanes to a titratable species. Then the less volatile components are pyrolyzed at a high temperature (800°C) in an O<sub>2</sub>-rich atmosphere.
- 11.3.2 Each column is pyrolyzed separately.
- 11.3.3 With the sample extractor, push the GAC packing onto the quartz boat attached to the analyzer.
- 11.3.4 Position sample boat for 2 minutes in the 200°C zone of pyrolysis tube.
- 11.3.5 Advance sample boat into 800°C zone of pyrolysis furnace. Allow sample boat to remain in the hot zone for 6 to 10 minutes until pyrolysis is complete.
- 11.4 Detection: Effluent gases from pyrolysis are directly analyzed in the micro-coulometric-titration cell. Sample results, in  $\mu\text{g Cl}^-$ , are either recorded on a strip chart recorder or presented in a direct, digital display.
- 11.5 Breakthrough
- 11.5.1 When TOX is detected on both front and back columns, TOX from the second column is called breakthrough. Ideally, TOX from the second column should not be more than 10% of the total TOX for the sample. If the TOX from the second column is greater than 10%, then one of three events could have happened:
- The first column was overloaded and a legitimate measure of breakthrough was obtained, and the sample should be diluted and reanalyzed.
  - Channeling or some other physical failure occurred and the sample should be reanalyzed.
  - The sample represents an out-of-control event and must be reanalyzed.

- 11.5.2 If, upon reanalysis (with or without dilution), the sample result indicates the TOX concentration for the second column is still greater than 10% of the total TOX and the inorganic chloride concentration is less than 20,000 times the organic chlorine value, then the result should be reported and noted in the data package case summary. If the second-column measurement is less than or equal to the nitrate-wash blank value, the second-column value should be disregarded.
- 11.5.3 Each sample must be analyzed in duplicate, and the results averaged for the final reporting value. A LCS sample will be analyzed before any field samples are analyzed and the acceptance range for LCS recovery is 80 to 120%. If the QCS results are outside the acceptance range, then the problem is identified and resolved and the instrument should be recalibrated before samples are analyzed.
- 11.5.4 Because the method is instrument-specific, a continuing calibration sample must be analyzed after every 20th field sample or at the end of sample analysis, whichever is more frequent. Continuing calibration samples are used to verify that the instrument is capable of providing acceptable data. A mid-level standard is typically used. The acceptance range for continuing calibration standard sample recovery is 90 to 110%. If the continuing calibration standard sample results are outside the acceptance range, then the problem is identified and resolved, and the samples since the last acceptable continuing calibration standard sample are reanalyzed.
- 11.5.5 One method blank is analyzed every 20 samples or one per analytical batch, whichever is more frequent.

## 12.0 Calculation

TOX is calculated using the formula:

$$\mu\text{g/L TOX} = \frac{(C_1 - C_3) + (C_2 - C_3)}{V}$$

Where:

$C_1$	=	Cl <sup>-</sup> in first column ( $\mu\text{g}$ )
$C_2$	=	Cl <sup>-</sup> in second column ( $\mu\text{g}$ )
$C_3$	=	Cl <sup>-</sup> in method (nitrate-wash) blank ( $\mu\text{g}$ )
V	=	sample volume (L)

### 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

### 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	1/20	90–110%	Recalibrate
LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75–125%	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

### 15.0 References

- 15.1 *Standard Methods for the Examination of Water and Wastewater*. 17th ed., Method 5320. 1989.

15.2 *Test Methods for Evaluating Solid Waste*. 3rd ed., SW-846, Method 9020.  
September 1986.

FERNALD/tox.51



## Color

**Working Linear Range:** With dilution, range is infinite.  
**Reporting Limit:** 5 units  
**Reporting Units:** Color units  
**Matrix:** Water

### 1.0 Scope and Application

The method is applicable to the measurement of water color derived from naturally occurring materials such as vegetable residues (leaves, bark, roots, humus, and peat materials) in ground, surface, and drinking water samples. It is not applicable to color measurements on waters containing highly colored industrial wastes.

### 2.0 Method Summary

The water sample is placed in a Nessler tube and visually compared to color standards in similar tubes. If the color exceeds the standard range, the sample may be diluted. **Note:** The method is pH-dependent.

### 3.0 Interferences

Turbidity interferes with visual comparison. Samples with turbidity should be clarified by centrifugation before color measurement.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.
- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

## 5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.

## 6.0 Apparatus

50-mL Nessler Tubes, matched, tall form, 50-mL-capacity.

## 7.0 Routine Preventive Maintenance

Examine Nessler tubes before each use to be sure that they are clean and have no cracks or scratches. Replace Nessler tubes as necessary.

## 8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Standard Chloroplatinate Solution: Dissolve 1.246 grams potassium chloroplatinate ( $K_2PtCl_6$ ) and 1 gram crystalline cobaltous chloride ( $CoCl_2 \cdot H_2O$ ) in water containing 100 mL of concentrated HCl. **Caution:** Heat-liberating reaction. Dilute to 1,000 mL with water. The standard is equivalent to 500 color units.

## 9.0 Standard Preparation

9.1 Prepare a series of standards by diluting aliquots of the standard chloroplatinate solution to 50 mL with water. These solutions can be prepared in the Nessler tubes.

<b>mL Standard Solution Diluted to 50 mL with Water</b>	<b>Color Units in Standard</b>
0.0	0
0.5	5
1.0	10
1.5	15
2.0	20
2.5	25
3.0	30
3.5	35
4.0	40
4.5	45
5.0	50
5.5	55
6.0	60
6.5	65
7.0	70

- 9.2 Once standard solutions are diluted, place an inert cap on Nessler tube to minimize volatilization and absorption of ammonia. It is not necessary to prepare all standard solutions, but since a standard calibration curve is not prepared, it may be helpful to prepare most, if not all, of them.

## 10.0 Sample Preparation

Allow samples to warm to room temperature. Measure and record the pH of each sample using Method FM-CON-0110.

## 11.0 Sample Analysis

### 11.1 Apparent Color

- 11.1.1 Fill Nessler tube to 50-mL mark with sample. Fill another Nessler tube with water to 50-mL mark.
- 11.1.2 Compare sample to standards and blank by looking vertically downward through tubes toward a white or specular surface placed at such an angle that light is reflected upward through columns of liquid.

11.1.3 If turbidity has not been removed, then report color as "apparent color." If color of sample exceeds 70 units, dilute sample until color is within range of standards.

## 11.2 True Color

11.2.1 Remove turbidity by centrifuging sample until supernatant is clear. The time required will depend upon the nature of the sample, the speed of the motor, and the radius of the centrifuge, but rarely will more than 1 hour be necessary.

11.2.2 Compare centrifuged sample to standards and blank by looking vertically downward through tubes toward a white or specular surface placed at such an angle that light is reflected upward through columns of liquid.

11.2.3 Report color as "true color." If color of sample exceeds 70 units, dilute sample until color is within range of standards.

## 12.0 Calculations

12.1 Calculate color units when dilution is required as:

$$\text{Color Units} = \frac{A \times 50}{V}$$

Where:

A = estimated color of diluted sample  
V = sample dilution (mL)

12.2 Results are reported in whole numbers as follows:

Color Units	Record to Nearest
1-50	1
51-100	5
101-250	10
251-500	20

### **13.0 Data Package Deliverables**

Color is a semiquantitative measure; therefore, a sample report indicating the identity of the sample and the results in color units are the only deliverables required for this analysis. The pH of each sample will also be provided with the sample results.

### **14.0 Quality Control (QC) Requirements**

Color is a semiquantitative measure; therefore, it is not necessary to analyze QC samples. Duplicate analyses are of little value since the sample result is based on visual comparison and is subject to individual variability.

### **15.0 Reference**

U.S. EPA. *Methods for the Chemical Analysis of Water and Wastes*. PB84-128677. Method 110.2.

FERNALD/color.51

FM-CON-0340

## Oxidation-Reduction Potential

3203

**Working Linear Range:** Instrument-dependent  
**Reporting Limits:** Instrument-dependent  
**Reporting Units:** mV  
**Matrix:** Water and wastes

### 1.0 Scope and Application

The method is applicable to drinking, surface, ground, and saline waters and domestic and industrial aqueous wastes.

### 2.0 Method Summary

Oxidation-reduction potential (ORP) is defined as the electromotive force developed by a platinum electrode immersed in a water sample relative to a standard reference electrode of known Eh. The obtained value is a crude estimate of the oxygen status of the sample. A positive value indicates that the water sample is in an oxidized state or that oxygen is present. A negative value would indicate an absence of oxygen or reducing conditions.

### 3.0 Interferences

- 3.1 ORP electrodes reliably measure ORP in nearly all aqueous solutions and in general are not subject to solution interference from color, turbidity, colloidal matter, and suspended matter.
- 3.2 The ORP of an aqueous solution is sensitive to pH variations when the oxidation-reduction reaction involves either hydrogen or hydroxyl ions. ORP generally tends to increase with an increase in hydrogen ions and to decrease with an increase in hydroxyl ions during such reactions.

### 4.0 Safety Precautions

- 4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the

procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

- 4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

#### **5.0 Sample Collection and Handling**

- 5.1 Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the Sitewide QAPjP.
- 5.2 The preferred method of obtaining ORP is in situ measurement. If this is impractical, measurements should be made immediately after the sample is collected in an appropriate container. Since exposure to the atmosphere may affect the ORP of the sample (oxygen may dissolve in water), precautions should be taken to minimize sample contact with the atmosphere before measurement of ORP.

#### **6.0 Apparatus**

- 6.1 Potentiometer or pH meter capable of mV measurements.
- 6.2 Standard Reference Electrode: Such as a saturated calomel electrode.
- 6.3 Platinum Electrode.
- 6.4 Thermometer: Capable of measuring 0° to 100°C ± 2°C.

#### **7.0 Routine Preventive Maintenance**

- 7.1 Perform routine preventive maintenance for the potentiometer and electrodes according to the manufacturers' directions.
- 7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the Sitewide QAPjP.

- 7.3 Check electrodes before each use for scratches and cracks, and replace as necessary.

## 8.0 Reagents and Calibration Standards

- 8.1 Water: All references to water assume the use of ASTM Type II water.

- 8.2 Ferrous-Ferric Reference Solution: Available commercially. Prepare by placing approximately 500 mL of water in a 1-liter volumetric flask. Weigh out and transfer to volumetric flask 39.21 grams of ferrous ammonium sulfate ( $\text{Fe}(\text{SO}_4) \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ), 48.22 grams of ferric ammonium sulfate ( $\text{FeNH}_4 \cdot (\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ ), and 56.2 mL of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ , specific gravity of 1.84), and swirl to mix. **Caution:** Heat-liberating reaction. Dilute to 1 liter. Use only reagent grade chemicals that have an assay confirming them to be within 1% of the nominal composition for preparing the standard. The solution can be stored in either a glass or plastic container. The ORP of the solution at 25°C using a saturated calomel reference electrode is 430 mV.

## 9.0 Calibration Procedure

Calibrate the meter according to the manufacturer's directions. Calibration can be checked using a reference solution different from the one used during calibration.

## 10.0 Sample Preparation

Sample preparation is not required. ORP is either measured in situ or immediately after placing a representative sample in a glass or plastic beaker.

## 11.0 Sample Analysis

- 11.1 Calibrate meter according to manufacturer's directions.
- 11.2 Insert platinum electrode and reference electrode into water sample and allow instrument to stabilize.
- 11.3 Note ORP of sample. Check and record sample temperature.

11.4 Remove electrode from sample and rinse with water.

## 12.0 Calculations

The ORP of the sample, in millivolts, can be referred back to the hydrogen scale ( $E_h$ ) using the calculation:

$$E_h = E_{obs} - E_{ref}$$

Where:

$E_h$  = ORP referred to the hydrogen scale (mV)

$E_{obs}$  = measured ORP (mV)

$E_{ref}$  = ORP of reference electrode as related to hydrogen electrode (mV)

## 13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Levels (ASLs) and the project-specific Sampling and Analysis Plan and are discussed in greater detail in the General Laboratory Requirements.

## 14.0 Quality Control (QC) Requirements

QC requirements are determined by the ASLs and the project-specific Sampling and Analysis Plan.

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ICVS	Begin	90–110%	Recalibrate
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LCS	Begin	80–120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

3203

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	data are qualified based on results using the data review and validation guidance, Section 11 of Sitewide QAPjP

**15.0 References**

- 15.1 *Annual Book of ASTM Standards*. Volume 11.01, Method 1498. 1990.
- 15.2 Russell Plumb, Jr. *Procedures for Handling and Chemical Analysis of Sediment and Water Samples*. Prepared for the U.S. EPA and the Army Corps of Engineers Technical Committee for Dredged and Fill Material. May 1981.

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