



**Techniques of Water-Resources Investigations  
of the United States Geological Survey**

**Chapter A1**

**METHODS FOR DETERMINATION  
OF INORGANIC SUBSTANCES  
IN WATER  
AND FLUVIAL SEDIMENTS**

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First Edition 1970  
Second Edition 1979  
Third Edition 1989

Book 5  
LABORATORY ANALYSIS

# Density, gravimetric

Parameter and Code:

Density I-1312-85 (g/mL at 20°C): 71820

## 1. Application

This method may be used to determine the density of any water from which the suspended sediment has been satisfactorily removed.

## 2. Summary of method

The density determination is based on the weight of a carefully measured volume of filtered sample at a given temperature. Densities are determined at 20°C, the same temperature at which volumetric glassware is calibrated.

## 3. Interferences

The only significant interference with this method is suspended sediment, which may usually be removed by filtration, centrifugation, or flocculation. Precautions should be taken to minimize evaporation during removal of sediment.

## 4. Apparatus

4.1 *Pipet*, volumetric, 50 mL calibrated: The actual volume delivery of the pipet is determined by weighing a delivering volume of demineralized water at 20°C. The volume is obtained from relative-density tables in handbooks. Alternatively, 50-mL pycnometer can be used; it must also be calibrated.

4.2 *Water bath*, constant temperature, 20 + 0.5°C.

4.3 *Weighing bottle*, 50-mL capacity.

## 5. Reagents

None required.

## 6. Procedure

6.1 Adjust the temperature of the filtered sample to 20.0°C.

6.2 Using a previously calibrated 50-mL pipet, transfer the sample to a tared weighing bottle.

6.3 Stopper the bottle immediately to prevent water loss by evaporation.

6.4 Weigh the solution to the nearest 0.1 mg.

## 7. Calculations

7.1 Determine density as follows:

$$\text{Density} = \frac{\text{g sample}}{\text{mL sample}}$$

7.2 If a constant-temperature bath is not available, the determination can be made at the sample temperature and a correction applied for the departure from 20°C. The temperature is recorded with an accurate thermometer, and the relative density for that temperature obtained from a table. The density result is then corrected by the factor:

$$\frac{\text{Relative density (20°C)}}{\text{Relative density (test temperature in°C)}}$$

## 8. Report

Report density (71820) to three decimal places in terms of grams per millimeter at 20°C.

## 9. Precision

Precision data are not available for this method, but results are believed reproducible to + 0.005 g/mL.

# Fluoride, colorimetric, zirconium-eriochrome cyanine R

## Parameters and Codes:

Fluoride, dissolved, I-1325-85 (mg/L as F): 00950

Fluoride, total, I-3325-85 (mg/L as F): 00951

Fluoride, suspended total I-7325-85 (mg/L as F): 82299

## 1. Application

1.1 This method may be used to analyze water, brines, and water-suspended sediment containing from 0.1 to 3.0 mg/L of fluoride. Higher concentrations need to be reduced by dilution. If the fluoride concentration exceeds 30 mg/L, determine fluoride by the ion-selective electrode method (I-1327).

1.2 Suspended total fluoride is calculated by subtracting dissolved fluoride from total fluoride.

1.3 The total fluoride in water-suspended sediment is determined after each sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn and then distilled.

## 2. Summary of method

2.1 The zirconium-eriochrome cyanine R method given here is a modified version of the procedure of Megregian (1954).

2.2 In acid solution, zirconium reacts with eriochrome cyanine R to form a read complex ion. Fluoride forms a more stable complex with zirconium ( $ZrF_6^{-2}$ ) and withdraws zirconium from the organic complex to produce a bleaching effect. Eriochrome cyanine R shows a decided specificity to zirconium.

2.3 The quality of the eriochrome cyanine R from different sources differs significantly, and it is necessary to test the reagent each time that it is prepared. The individual absorbance curves show corresponding differences, and the sensitivity of fluoride between reagents may differ by 20 percent.

2.4 The method includes a distillation step to decompose organic fluoride compounds and

attack minerals such as fluor spar in water-suspended sediment. Samples that contain a high concentration of dissolved solids need to be distilled. The method also eliminates interferences noted below. A fixed volume of sample is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

## 3. Interferences

3.1 Under the experimental conditions, the dye does not give a color with titanium or beryllium, two metals that react with many other zirconium agents. Aluminum decreases the apparent fluoride concentration. This interference is eliminated by allowing the solution to stand for at least 2 h before measuring the absorbance. As much as 10,000  $\mu\text{g/L}$  of aluminum can be tolerated.

3.2 Analytical conditions are not overly critical. The pH is controlled at a highly acid level by the addition of 1.7 mL of concentrated hydrochloric acid to each sample. This assures that high concentrations of bicarbonate or other alkaline ions will not affect the pH significantly. Sulfate interferes but is removed by precipitation as barium sulfate. Overnight standing is usually required to ensure complex settling of barium sulfate before measuring the absorbance. The clarification of the sample can be accelerated by centrifuging if immediate results are required. Filtration should not be used because of loss of color by adsorption on the filter medium.

3.3 Residual chlorine, chromate, and probably other strong oxidants attack the dye.

Stannous chloride is used to eliminate chromate and chlorine interference. Chromium, cadmium, and nickel, in concentrations of less than 5,000  $\mu\text{g/L}$ , do not interfere. When the fluoride concentration exceeds 1.0 mg/L, larger quantities of these metals can be tolerated. Ten mg/L of cyanide or phosphate and 10,000  $\mu\text{g/L}$  of iron, or zinc, or lead cause no appreciable interference if the sample is allowed to stand overnight.

3.4 The determination shows "salt effect"; the sensitivity is depressed by 5–10 percent at a dissolved-solids concentration of 10,000 mg/L. The effect of the usual type of color is not serious. A color of 70 on the platinum-cobalt scale is equivalent to an absorbance error of only 0.005 in the spectrophotometric measurement. Thus, it appears that color correction will not often be necessary. Highly colored or highly mineralized samples need to be distilled.

3.5 The method has rather good tolerance for temperature differences. For most purposes, operating at room temperature without other precautions is satisfactory.

#### 4. Apparatus

4.1 *Distillation assembly* (fig. 24), consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer, 250°C.

4.2 *Spectrometer*, for use at 540 nm, and cells with a minimum light-path length of 4 cm.

#### 5. Reagents

5.1 *Eriochrome cyanine R solution*, 0.90 g/100 mL: Dissolve 1.80 g tested eriochrome cyanine R in water and dilute to 200 mL. The National Aniline Co. product labeled "alizarol cyanine RC" has been used successfully. A precipitate sometimes forms when the solution is prepared, but the solution may be filtered prior to use.

5.2 *Fluoride standard solution I*, 1.00 mL = 0.10 mg  $\text{F}^{-1}$ : Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride standard solution II*, 1.00 mL = 0.01 mg  $\text{F}^{-1}$ : Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.4 *Hydrochloric acid*, 6M: Mix 50 mL concentrated HCl (sp gr 1.19) with demineralized water and dilute to 100 mL.

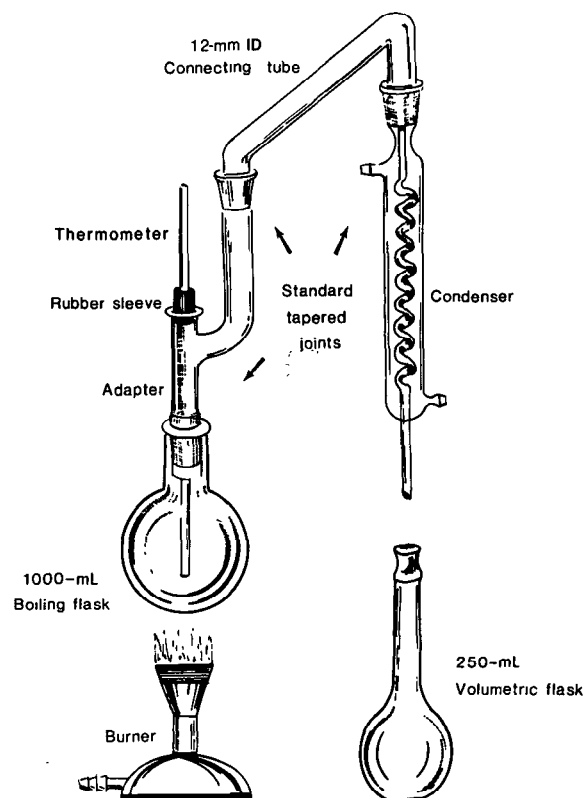


Figure 24.—Fluoride, distillation assembly

5.5 *Mixed indicator solution*: To about 300 mL demineralized water, add 20.0 mL eriochrome cyanine R solution and 10.0 mL  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  solution. Add 70 mL concentrated HCl (sp gr 1.19) and 4 g  $\text{BaCl}_2$ . Dissolve and dilute to 1,000 mL with demineralized water.

NOTE 1. It is practical to prepare more than 1 L of mixed indicator solution at a time. Eighteen liters, contained in a 5-gallon reagent bottle, seems to be a practical volume. If this volume is prepared, the component solutions must be prepared in correspondingly larger volumes.

NOTE 2. Once prepared, the mixed indicator solution should be allowed to stand for about 1 week in order to permit any precipitate to settle to the bottom of the bottle. The reagent is then used without disturbing the precipitate.

5.6 *Silver sulfate*, powder.

5.7 *Stannous chloride solution*, 1.7 g/100 mL: Dissolve 1.0 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  in 10 mL concentrated HCl (sp gr 1.19) and dilute to 50

mL with demineralized water. This solution is unstable. Prepare fresh daily.

5.8 *Sulfuric acid, concentrated* (sp gr 1.84).

5.9 *Zirconyl nitrate solution*, 0.21 g/100 mL: Dissolve 0.49 g  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  in 200 mL 6M HCl.

## 6. Procedure

### 6.1 *Distillation:*

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated  $\text{H}_2\text{SO}_4$ . Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180 °C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL well-mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL of distillate has been collected, and the temperature of the acid mixture has returned to 180 °C. When the temperature of the acid mixture at the completion of the distillation exceeds 183 °C, add 50 mL demineralized water and distill the mixture until the temperature again reaches 180 °C. After distilling a high-fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL of water. This prevents a carryover of fluoride in subsequent samples. When samples with high-chloride content are to be distilled,  $\text{Ag}_2\text{SO}_4$  should be added to the distilling flask in proportion of 5 mg per milligram of  $\text{Cl}^-$ .

### 6.2 *Colorimetric procedure:*

6.2.1 Pipet a volume of filtered sample or a volume of the cooled distillate (step 6.1.4) containing less than 0.03 mg  $\text{F}^-$  (10.0 mL max) into a 50-mL centrifuge tube or test tube.

6.2.2 Prepare a blank and sufficient standards, and adjust the volume of each to 10.0 mL.

6.2.3 If chromate, residual chlorine, or other strong oxidizing agents are present in the sample, add 0.1 mL  $\text{SnCl}_2$  solution and let the solution stand for 10 minutes.

6.2.4 Add 25.0 mL mixed indicator solution.

6.2.5 Allow the solution to stand overnight for barium sulfate to settle.

6.2.6 Decant approximately 25 mL clear supernatant solution, taking care not to disturb the precipitate.

6.2.7 Determine the absorbance of each sample and standard against the blank, which is set at an absorbance of 1.50 (NOTE 3); when necessary, make correction for water color.

NOTE 3. Alternatively, measurement of transmittance may allow some instruments to be calibrated so that concentration can be read directly.

## 7. Calculations

7.1 Determine milligrams of fluoride in each sample solution from a plot of absorbances of standards.

7.2 Determine the dissolved or total-fluoride concentration in milligrams per liter as follows:

$$F \text{ (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mg F in sample}$$

7.3 To determine milligrams per liter of suspended total fluoride, subtract dissolved-fluoride concentration from total-fluoride concentration.

## 8. Report

Report fluoride, dissolved (00950), total (00951), and suspended-total (82299), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved fluoride for 30 samples within the range of 0.3 to 3.7 mg/L may be expressed as follows:

$$S_T = 0.118X + 0.006$$

where

$S_T$  = overall precision, milligrams per liter, and

$X$  = concentration of fluoride, milligrams per liter.

The correlation coefficient is 0.8048.

9.2 Precision for dissolved fluoride for four of the 30 samples expressed in terms of the percent relative standard deviation is as follows:

<u>Number of laboratories</u>	<u>Mean (mg/L)</u>	<u>Relative standard deviation (percent)</u>
34	0.30	17
17	1.06	7
3	2.00	15
9	3.69	13

9.3 It is estimated that the percent relative standard deviation for total and suspended

total fluoride will be greater than that reported for dissolved fluoride.

#### References

- Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530-5.
- Megregian, Stephen, 1954, Rapid spectrophotometric determination of fluoride with zirconium-eriochrome cyanine R lake: Analytical Chemistry, v. 26, p. 1161-66.

# Fluoride, electrometric, ion-selective electrode

## Parameter and Code:

Fluoride, dissolved, I-1327-85 (mg/L as F): 00950

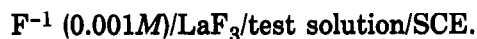
### 1. Application

This method is applicable to the measurement of dissolved fluoride in finished water, natural water, brines, and industrial wastewater. Concentrations of at least 0.1 mg/L can be determined. Samples containing more than 3 mg/L of fluoride need to be diluted.

### 2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE), and a pH meter having an expanded millivolt scale (Frant and Ross, 1968).

2.2 The fluoride electrode consists of a laser-type doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:



### 3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity, so that high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of the buffer solution, which contains a high concentration of dissolved solutes, effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, hydrofluoric acid is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The

addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include iron(III), aluminum(III), and silicon dioxide. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes as much as to 10,000  $\mu\text{g}$  iron(III), 2,000  $\mu\text{g}$  aluminum(III), and 100 mg silicon dioxide.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

### 4. Apparatus

4.1 *Fluoride ion-selective electrode.*

4.2 *pH meter, with expanded scale.*

4.3 *Reference electrode, standard calomel, sleeve-type.*

4.4 *Stirrer, magnetic, Teflon-coated stirring bar.*

### 5. Reagents

5.1 *Buffer solution, pH 5.0 to 5.5:* To approx 500 mL demineralized water in a 1-L beaker, add 57 mL glacial  $\text{HC}_2\text{H}_3\text{O}_2$ , 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution to between 5.0 and 5.5 with 5M NaOH (about 170 mL will be required). Dilute to 1 L with demineralized water.

5.2 *Fluoride standard solution I, 1.00 mL = 0.10 mg  $\text{F}^{-1}$ :* Dissolve 0.2210 g NaF in demineralized water and dilute to 1,000 mL.

5.3 *Fluoride standard solution II*, 1.00 mL = 0.01 mg F<sup>-1</sup>: Dilute 100 mL fluoride standard solution I to 1,000 mL with demineralized water.

## 6. Procedure

6.1 Adjust pH meter according to manufacturer's instructions.

6.2 Pipet 25.0 mL sample into 100-mL beaker.

6.3 Prepare a series of four standards containing 0.1, 1.0, 2.0, and 3.0 mg/L F<sup>-1</sup>, and pipet 25.0 mL of each into 100-mL beakers.

6.4 Add 25.0 mL buffer solution to each sample and standard.

6.5 Place beaker on magnetic stirrer, immerse electrodes, and measure potential while mixing. The electrodes must remain in the solution until reading has stabilized. This may require 5 min or more.

## 7. Calculations

7.1 Construct a graph of potential in millivolts (mV) versus concentration of standards (mg/L) on semilog paper, with the concentrations plotted on the logarithmic axis.

7.2 From the graph, determine the milligrams per liter of fluoride in each sample.

## 8. Report

Report fluoride, dissolved (00950), concen-

trations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

9.1 The standard deviation for dissolved fluoride within the range of 0.03 to 2.14 mg/L for 27 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.14 mg/L ranged from 0.135 to 0.153 mg/L.

9.2 Precision for dissolved fluoride for five of the 27 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
16	0.03	167
6	.32	41
13	.55	35
16	1.01	15
17	2.14	11

## References

- Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water samples: *Analytical Chemistry*, v. 40, p. 1169-71.
- Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: *Water Research*, v. 3, p. 273-80.



# Fluoride, electrometric, ion-selective electrode, automated-segmented flow

## Parameters and Codes:

Fluoride, dissolved, I-2327-85 (mg/L as F): 00950  
Fluoride, total, I-4327-85 (mg/L as F): 00951  
Fluoride, suspended total, I-7327-85 (mg/L as F): 82299

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.1 to 3.0 mg/L of fluoride with conductivities less than 20,000  $\mu\text{S}/\text{cm}$ . Samples with higher conductivities need to be distilled.

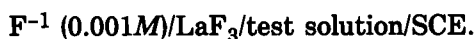
1.2 Suspended total fluoride is calculated by subtracting dissolved fluoride from total fluoride.

1.3 Total fluoride in water-suspended sediment is determined after each sample is shaken vigorously and a suitable aliquot of well-mixed sample is rapidly withdrawn and then distilled.

## 2. Summary of method

2.1 Fluoride is determined potentiometrically in a buffered sample with use of an ion-selective (fluoride) electrode in conjunction with a standard calomel reference electrode (SCE) and with a pH meter having an expanded millivolt scale (Frant and Ross, 1968; Harwood, 1969; Bellack, 1958).

2.2 The fluoride electrode consists of a laser-type, doped lanthanum fluoride crystal, across which a potential is developed by fluoride ions. The cell may be represented by:



This electrode deteriorates in time and must be replaced when results become erratic.

2.3 The method includes a distillation step to decompose organic fluoride compounds and attack minerals such as fluor spar in water-suspended sediment. A fixed volume of sample

is added to a sulfuric acid solution having a specific boiling point and is distilled until an identical volume is recovered (Bellack, 1958). The fluoride is distilled as fluosilicic acid.

## 3. Interferences

3.1 The ion-selective electrode measures fluoride-ion activity; thus, high concentrations of dissolved solutes (which lower the ion-activity coefficient) cause an error in the determination. Addition of a buffer solution that contains a high concentration of dissolved solutes effectively masks minor variations in the salt content of the samples and, therefore, minimizes this error.

3.2 The optimum pH for measurement is between 5.0 and 8.5. Below this range, hydrofluoric acid is only slightly dissociated, and above a pH of 8.5, hydroxyl ion interferes. The addition of the buffer solution will adjust the pH of most samples to between 5.0 and 5.5.

3.3 Several polyvalent cations capable of complexing fluoride ion interfere. These include iron(III), aluminum(III), and silicon dioxide. The extent of their interference is proportional to their concentration, so that dilution of the sample with an equal volume of buffer solution reduces the interference. The (1,2-cyclohexylenedinitrilo)tetraacetic acid (CDTA) in the buffer solution complexes up to 10,000  $\mu\text{g}$  iron(III), 2,000  $\mu\text{g}$  aluminum(III), and 100  $\mu\text{g}$  silicon dioxide.

3.4 Orthophosphate-phosphorus concentrations of 25 mg/L and sulfate and chloride concentrations of 3,000 mg/L do not interfere (Harwood, 1969).

#### 4. Apparatus

4.1 *Distillation assembly*, (fig. 25), consisting of a round-bottom distilling flask, adapter, connecting tube, condenser, receiving flask, and thermometer (250 °C).

4.2 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, heating bath, recorder, potentiometer, and printer.

4.3 *Fluoride ion-selective electrode*.

4.4 *Reference electrode*, standard calomel.

4.5 With this equipment a 40/h (2/1) cam has been found satisfactory for the range from 0.1 to 3.0 mg/L.

#### 5. Reagents

5.1 *Brij-35 solution*: 30-percent aqueous solution (Baker Cat. No. C 706 or equivalent).

5.2 *Buffer solution*, 0.33 mg/L, pH 5.0 to 5.5: To approx 500 mL demineralized water in a 1-L beaker, add 57 mL glacial  $\text{HC}_2\text{H}_3\text{O}_2$ , 58 g NaCl, and 4.5 g (1,2-cyclohexylenedinitrilo) tetraacetic acid (CDTA). Stir to dissolve and cool to room temperature. Adjust the pH of the solution between 5.0 and 5.5 with 5M NaOH (about 170 mL will be required). Filter if necessary and add 33 mL of fluoride standard solution II and 0.5 mL of Brij-35 solution. Dilute to 1,000 mL with demineralized water.

5.3 *Fluoride standard solution I*, 1.00 mL = 1.00 mg F: Dissolve 2.2101 g NaF in demineralized water and dilute to 1,000 mL.

5.4 *Fluoride standard solution II*, 1.00 mL = 0.01 mg F: Dilute 10.0 mL fluoride standard solution I to 1,000 mL with demineralized water.

5.5 *Fluoride working standards*: Prepare a blank and 500 mL each of a series of fluoride working standards by appropriate quantitative dilution of fluoride standard solution II as follows:

Fluoride standard solution (mL)	Fluoride concentration (mg/L)
0.0	0.0
10.0	.20
25.0	.50
50.0	1.00
75.0	1.50
100.0	2.00
125.0	2.50
150.0	3.00

5.6 *Silver sulfate*, powder.

5.7 *Sulfuric acid*, concentrated (sp gr 1.84).

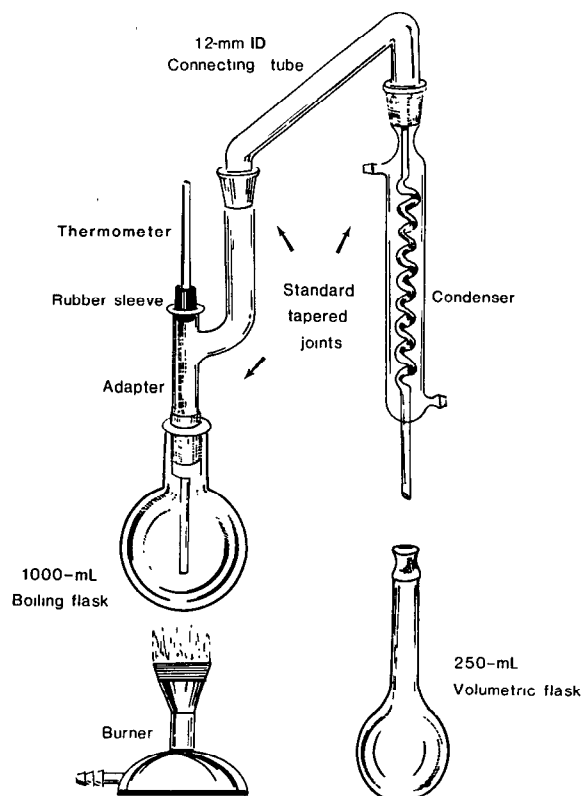


Figure 25.—Fluoride, distillation assembly

#### 6. Procedure

6.1 *Distillation procedure*: Water-suspended sediment needs to be distilled. The distillation may be omitted for samples for determining dissolved fluoride if the specific conductance is less than 20,000  $\mu\text{S}/\text{cm}$ .

6.1.1 Place 400 mL demineralized water in a 1-L distilling flask containing a few glass beads. *Cautiously*, and with constant swirling, add 200 mL concentrated  $\text{H}_2\text{SO}_4$ . Connect the flask to the condenser assembly and distill until the temperature of the acid mixture reaches 180 °C. At this point the proper acid concentration has been reached. The acid need not be replaced until the accumulation of nonvolatile material is sufficient to cause interference. An occasional recovery check with a standard fluoride sample will indicate the need for replacement.

6.1.2 Cool to room temperature.

6.1.3 *Cautiously*, and with constant swirling, add 250 mL of well-mixed sample to the acid mixture in the distillation flask.

6.1.4 Distill until 250 mL distillate has been collected and the temperature of the acid

mixture has returned to 180°C. When the temperature of the acid mixture at the completion of the distillation exceeds 183°C, add 50 mL distilled water and distill the mixture until the temperature again reaches 180°C. After distilling a high fluoride sample (3 mg/L or more), clean the apparatus by distilling 250 mL water. This prevents a carryover of fluoride in subsequent samples. When samples with high chloride content are to be distilled, AgSO<sub>4</sub> should be added to the distilling flask in proportion of 5 mg per milligram of Cl<sup>-1</sup>.

### 6.2 *Electrometric procedure:*

6.2.1 Set up manifold (fig. 26).

6.2.2 Allow potentiometer, recorder, and heating bath to warm up for at least 30 min or until the temperature of the heating bath reaches 37°C.

6.2.3 Calibrate the potentiometer according to the manufacturer's instructions.

6.2.4 Adjust the baseline to read 10 scale divisions on the recorder with all reagents, but with demineralized water in the sample line.

6.2.5 Place a complete set of standards in the first positions of the first sample tray, beginning with the most concentrated working standard

(the first two positions should both contain 3-mg/L standards). Place individual standards of differing concentrations in every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each sample tray with unknown samples.

6.2.6 Begin analysis. When the peak from the second 3-mg/L standard appears on the recorder, adjust the STD CAL control until the flat portion of the peak reads 100 scale divisions.

### 7. Calculations

7.1 Prepare an analytical curve by plotting the height of each standard peak versus its respective fluoride concentration. This curve should be linear or very nearly linear.

7.2 Compute the concentration of dissolved or total fluoride in each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine milligrams per liter of suspended total fluoride, subtract dissolved-fluoride concentration from total-fluoride concentration.

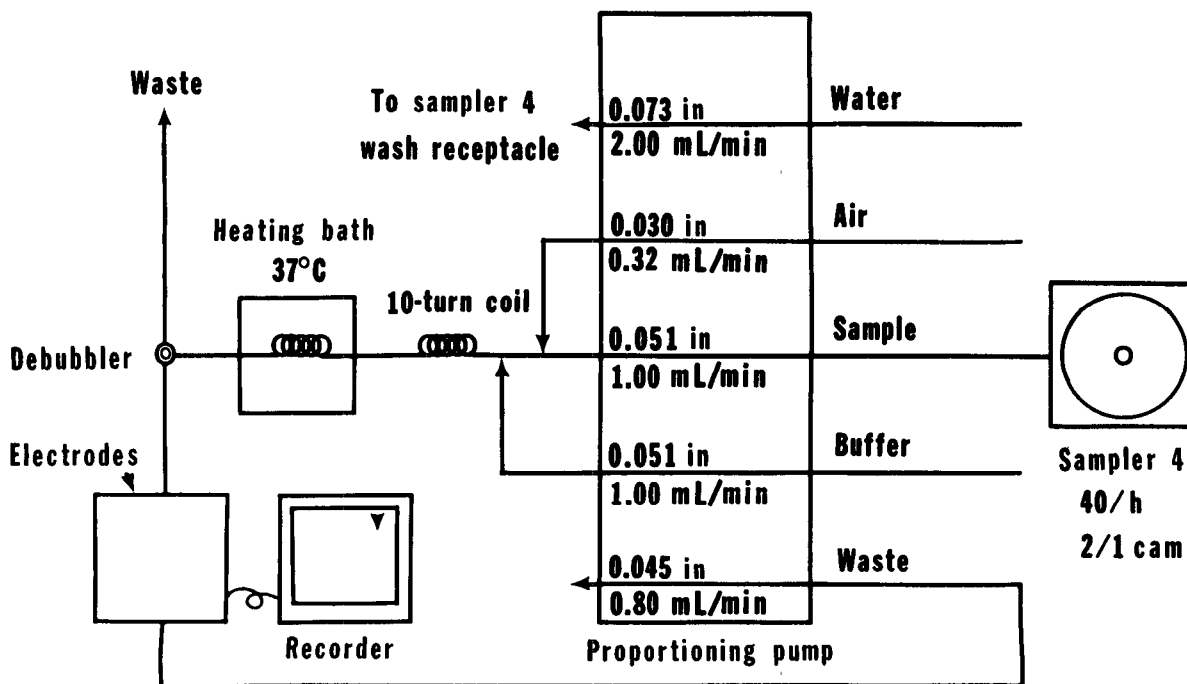


Figure 26.—Fluoride, ion-selective electrode manifold

**8. Report**

Report fluoride, dissolved (00950), total (00951), and suspended-total (82299), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

**9. Precision**

9.1 The standard deviation for dissolved fluoride within the range of 0.33 to 1.28 mg/L for nine samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 0.07 mg/L ranged from 0.05 to 0.09 mg/L.

9.2 Precision for dissolved fluoride for three of the nine samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.33	18
8	1.09	6
4	1.28	7

9.3 It is estimated that the percent relative standard deviation for total and suspended total fluoride will be greater than that reported for dissolved fluoride.

**References**

- Bellack, Ervin, 1958, Simplified fluoride distillation method: American Water Works Association Journal, v. 50, p. 530-5.
- Erdmann, D.E., 1975, Automated ion-selective method for determining fluoride in natural waters: Environmental Science and Technology, v. 9, p. 252-3.
- Frant, M. S., and Ross, J. W., Jr., 1968, Use of a total ionic strength adjustment buffer for electrode determination of fluoride in water supplies: Analytical Chemistry, v. 40, p. 1169-71.
- Harwood, J. E., 1969, The use of an ion-selective electrode for routine fluoride analysis on water samples: Water Research, v. 3, p. 273-80.

## Fluoride, ion-exchange chromatographic, automated

### Parameters and Codes:

Fluoride, dissolved, I-2057-85 (mg/L as F): 00950

Fluoride, dissolved, I-2058-85 (mg/L as F): 00950

### 2. Summary of method

Fluoride is determined sequentially with six other anions by ion-exchange chromatography. Ions are separated based on their affinity for the exchange sites of the resin. The separated

anions in their acid form are measured using an electrical-conductivity cell. See method I-2057, anions, ion-exchange chromatographic, automated, and method I-2058 anions, ion-exchange chromatographic, precipitation, automated.

## Hardness, calculation

Parameter and Code:

Hardness, I-1340-85 (mg/L as CaCO<sub>3</sub>): 00900

### 1. Application

This method may be used to calculate hardness for any sample for which determined values for barium, calcium, strontium, and magnesium are available.

### 2. Summary of method

Hardness is computed from the individual determinations of the alkaline earths. This is best accomplished by summing the milliequivalents per liter of calcium, magnesium, strontium, and barium. In many cases the contributions of strontium and barium are insignificant compared to those of calcium and magnesium and can safely be ignored.

### 7. Calculations

Hardness as mg/L CaCO<sub>3</sub> =

$$\sum \text{me/L}(\text{Ca} + \text{Mg} + \text{Ba} + \text{Sr}) \times 50.05.$$

### 8. Report

Report hardness, calculated, as CaCO<sub>3</sub> (00900), concentrations as follows: less than 10 mg/L, whole numbers, 10 mg/L and above, two significant figures.

### 9. Precision

Precision data are not available for this method, but reproducibility should be comparable to those of the individual determinations.

# Hardness, titrimetric, complexometric

## Parameter and Code:

Hardness I-1338-85 (mg/L as CaCO<sub>3</sub>): 00900

### 1. Application

This procedure is applicable to most natural and treated water, but the method fails conspicuously at times with acidic or polluted water that contains excessive amounts of heavy metals.

### 2. Summary of method

2.1 Disodium dihydrogen ethylenediaminetetraacetate (Na<sub>2</sub>EDTA) forms a slightly ionized, colorless, stable complex with alkaline-earth ions. The indicator Eriochrome Black T is bright blue in the absence of alkaline earths, but with them forms a deep-red complex that has a higher ionization constant than that of the Na<sub>2</sub>EDTA complex. Hence, with Eriochrome Black T as an indicator, the alkaline earth can be titrated with Na<sub>2</sub>EDTA.

2.2 All alkaline earths titrate approximately stoichiometrically. The titration should proceed immediately upon addition of the indicator, because the color of the solution fades after standing. The optimum pH of the titration is 10.4 or above.

2.3 Additional information on the principle of the determination is given by Goetz and others (1950), and by Botha and Webb (1952).

### 3. Interferences

3.1 The salt Na<sub>2</sub>EDTA also forms stable complexes with iron, manganese, copper, lead, cobalt, zinc, and nickel. Heavy-metal interferences can usually be eliminated by complexing the metals with cyanide. In the presence of cyanide, the procedure can be used to analyze undiluted samples having iron, copper, zinc, or lead concentrations as high as 10 mg/L.

3.2 The higher oxidation states of manganese than manganese(II) react rapidly with the

indicator to form discolored oxidation products. Hydroxylamine hydrochloride reagent is used to reduce manganese to the divalent state. The divalent manganese interference can be removed by addition of one or two small crystals of potassium ferrocyanide.

3.3 In the presence of high aluminum concentrations, a characteristic effect will be observed as the end point is approached. The blue color that indicates the end point will appear and then, after short standing, will revert to red. The reversion should not be confused with the gradual change that normally takes place in the titrated sample several minutes after the titration has been completed.

### 4. Apparatus

Visual-titration assembly: Some analysts prefer to use conventional lighting and hand stirring. Others report better results by using a visual-titration assembly consisting of a motor-driven stirrer, 25-mL buret, white-porcelain-base buret holder, and shaded incandescent lamp. The sample beaker is placed near the front of the porcelain base, and the reaction is viewed diagonally downward through the side of the beaker and against the white background. Illumination is from behind the beaker.

### 5. Reagents

5.1 *Ammonium hydroxide, concentrated* (sp gr 0.900).

5.2 *Calcium standard solution*, 1.00 mL = 1.00 mg CaCO<sub>3</sub>: Suspend 1.000 g CaCO<sub>3</sub>, dried at 180°C for 1.0 h, in approx 600 mL demineralized water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with demineralized water.

5.3 *Eriochrome Black T indicator solution*, 0.4 g/L: Dissolve 0.40 g Eriochrome Black T in 100 mL demineralized water and dilute to 1 L with 95-percent ethanol. This indicator is stable for at least 2 months. The Eastman Kodak Co. reagent has been found to be satisfactory.

5.4 *Hydroxylamine hydrochloride solution*, 30 g/L: Dissolve 30 g  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in demineralized water and dilute to 1 L.

5.5 *Potassium ferrocyanide*, crystals.

5.6 *Sodium cyanide solution*, CAUTION: NaCN is a deadly poison, and the reagent solution must be so marked, 2.5 g/100 mL: Dissolve 2.5 g NaCN in demineralized water and dilute to 100 mL.

5.7 *Na<sub>2</sub>EDTA standard solution*, 1.00 mL  $\phi$  1.00 mL mg  $\text{CaCO}_3$ : Dissolve 3.72 g  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$ , dried overnight in a  $\text{H}_2\text{SO}_4$  desiccator, in demineralized water and dilute to 1,000 mL. The reagent is stable for several weeks and a larger volume is usually prepared. Check the titer of the reagent by titrating 25.0 mL calcium standard solution as described in the procedure for sample analysis.

## 6. Procedure

6.1 Pipet a volume of sample containing less than 25 mg hardness (50.0 mL max) into a 150-mL beaker, and adjust the volume to approx 50 mL.

6.2 Insert the beaker in the titration assembly and start the stirrer.

6.3 Add 1 mL  $\text{NH}_2\text{OH}\cdot\text{HCl}$  solution.

6.4 Add 1 mL concentrated  $\text{NH}_4\text{OH}$ . (If not tightly stoppered, it tends to lose strength, and 1 mL of weak  $\text{NH}_4\text{OH}$  will not buffer the solution to the desired pH).

6.5 Add 2 mL NaCN solution—CAUTION: deadly poison. The addition of NaCN may be omitted if copper, zinc, lead, cobalt, and nickel are entirely absent, and if the sample contains less than 0.25 mg Fe and 0.025 mg Mn.

6.6 If manganese is present, add one or two small crystals of  $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ . Stir and wait at least 5 min until the  $\text{Mn}_2\text{Fe}(\text{CN})_6$  precipitates.

6.7 Add 2.0 mL Eriochrome Black T indicator solution.

6.8 Titrate with  $\text{Na}_2\text{EDTA}$  standard solution until blue or purple swirls begin to show. The end point is reached when all traces of red

and purple have disappeared and the solution is clear blue. The change in color occurs rapidly; so the end point of the titration must be approached cautiously.

## 7. Calculations

Hardness,

$$\text{as CaCO}_3 \text{ (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mL titrant}$$

## 8. Report

Report hardness, as  $\text{CaCO}_3$  (00900), as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

## 9. Precision

9.1 Precision for hardness for 37 samples within the range of 3.2 to 312 mg/L may be expressed as follows:

$$S_T = 0.041X + 0.310$$

where

$S_T$  = overall precision, milligrams per liter, and

$X$  = concentration of hardness, milligrams per liter as  $\text{CaCO}_3$ .

The correlation coefficient is 0.8105.

9.2 Precision for hardness for six of the 31 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
14	3.22	90
11	4.50	7
8	50.5	3
14	105	3
8	232	3
11	312	4

## References

- Botha, C. R., and Webb, M. M., 1952, The versenate method for the determination of calcium and magnesium in mineralized waters containing large concentrations of interfering ions: Institute of Water Engineers Journal, v. 6.
- Goetz, A., Loomis, T. C., and Diehl, H., 1950, Total hardness in water—the stability of standard disodium dihydrogen ethylenediamine tetraacetate solutions: Analytical Chemistry, v. 22, p. 798-9.



## Hardness, noncarbonate, calculation

### Parameter and Code:

Hardness, noncarbonate I-1344-85 (mg/L as CaCO<sub>3</sub>): 00902

#### 1. Application

This method may be used to compute noncarbonate hardness for any water for which determined values are available for hardness and alkalinity.

#### 2. Summary of method

Noncarbonate hardness is computed from the hardness and alkalinity determinations (methods I-1340 and I-1030 or I-2030). No negative values are reported. However, "negative noncarbonate hardness" will counteract "positive noncarbonate hardness" in a mixture of two or more waters. Hence, in all calculations of averages concerned with a mixture of waters for which two or more analyses are available, noncarbonate hardness of the resulting mixtures must be computed from the average

hardness and average alkalinity and not from the average of the noncarbonate hardnesses of the individual samples.

#### 7. Calculations

Hardness, noncarbonate, as mg/L CaCO<sub>3</sub> = (me/L hardness - me/L alkalinity) × 50.05

#### 8. Report

Report hardness, noncarbonate, calculated as CaCO<sub>3</sub> (00902), concentrations as follows: less than 10 mg/L, whole numbers; 10 mg/L and above, two significant figures.

#### 9. Precision

Precision data are not available for this method, but reproducibility should be comparable to that of the individual determinations.

# Iodide, colorimetric, ceric-arsenious oxidation

## Parameter and Code:

Iodide, dissolved, I-1371-85 (mg/L as I): 71865

### 1. Application

This method may be used to determine iodide in fresh water and brines containing from 0.001 to 0.060 mg/L of iodide. Greater concentrations need to be reduced by dilution; however, samples containing concentrations greater than 1 mg/L need to be analyzed by the bromine oxidation method (method I-1370).

### 2. Summary of method

This method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. The reaction may be stopped completely at any time by the addition of silver ion. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

### 3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Low values for iodide may result if the reaction test tubes are not clean. Rinsing each sample tube with hydrochloric acid, followed by deionized water immediately before use, removes possible contaminants.

3.3 Bromide ion does not interfere, and any substance that oxidizes iodide to iodine has no effect on the reaction.

3.4 Certain phosphate compounds used in water treatment, such as Calgon, have an inhibiting effect on the reaction. This effect can be eliminated by adding 3 drops concentrated

nitric acid at step 6.1 in the procedure. The nitric acid should be aerated to remove nitrogen oxides.

### 4. Apparatus

4.1 *Stirring rods*, glass.

4.2 *Water bath*, constant-temperature ( $30 \pm 0.5^\circ\text{C}$ ).

4.3 *Spectrometer* for use at 450 nm.

4.4 Refer to manufacturer's manual to optimize instrument.

### 5. Reagents

5.1 *Arsenious acid standard solution*, 0.3N  $\text{H}_3\text{AsO}_3$ : Add 14.84 g primary standard  $\text{As}_2\text{O}_3$  to 500 mL demineralized water in a 1,000-mL beaker. Next, add slowly 28 mL concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84); stir and warm the mixture until the  $\text{As}_2\text{O}_3$  is dissolved. Cool, transfer to a 1,000-mL volumetric flask, and dilute to volume with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate standard solution*, 0.1N  $\text{Ce}(\text{HSO}_4)_4$ : Dissolve 52.80 g anhydrous  $\text{Ce}(\text{HSO}_4)_4$  in 600 mL 2.5M  $\text{H}_2\text{SO}_4$  contained in a 1000-mL volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained. Cool and dilute to volume with 2.5M  $\text{H}_2\text{SO}_4$ .

5.3 *Iodide standard solution I*, 1.00 mL = 0.100 mg  $\text{I}^{-1}$ : Dissolve 0.1308 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide standard solution II*, 1.00 mL = 0.010 mg  $\text{I}^{-1}$ : Dilute 100 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Iodide standard solution III*, 1.00 mL = 0.0001 mg  $\text{I}^{-1}$ : Dilute 10.0 mL iodide

standard solution II to 1,000 mL with demineralized water.

5.6 *Silver nitrate solution*, 0.10 g/L: Dissolve 0.10 g AgNO<sub>3</sub> in 1 L demineralized water. Store in a dark bottle.

5.7 *Sulfuric acid*, 2.5M: *Cautiously* add 139 mL concentrated H<sub>2</sub>SO<sub>4</sub> (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

## 6. Procedure

6.1 Pipet a volume of sample containing less than 0.0012 mg I<sup>-1</sup> (20.0 mL max) into a 23-mm absorption cell.

6.2 Prepare a demineralized water blank to be used as a control and sufficient standards containing less than 0.0012 mg I<sup>-1</sup> in 23-mm absorption cells.

6.3 Dilute each sample, blank, and standard to 20.0 mL with demineralized water; add 0.5 mL concentrated H<sub>2</sub>SO<sub>4</sub> to each and mix.

6.4 Add 1.0 mL H<sub>3</sub>AsO<sub>3</sub> standard solution to each absorption cell and mix.

6.5 Place all absorption cells in a constant-temperature bath at 30°C. Allow 30 to 45 min for the contents to reach temperature equilibrium.

6.6 At zero time, add 1.0 mL Ce(HSO<sub>4</sub>)<sub>4</sub> standard solution (temperature equilibrated) and mix.

6.7 After exactly 10 min add, with stirring, 1 drop (0.05 mL) AgNO<sub>3</sub> solution (NOTE 1). NOTE 1. The addition of AgNO<sub>3</sub> solution may be omitted if the ceric sulfate solution is added at intervals of 30 sec or longer and the absorbance of each sample, blank, and standard measured exactly 10.0 min after the addition of the Ce(HSO<sub>4</sub>)<sub>4</sub> solution.

6.8 Measure the absorbance of each blank, standard, and sample at 450 nm, using demineralized water as a reference.

## 7. Calculations

7.1 Construct an analytical curve by plotting the ratio  $A_s/A_c$  against milligrams of iodide on semilog paper ( $A_s$  = absorbance of standard and  $A_c$  = absorbance of control).

7.2 From the curve, determine the milligrams of iodide corresponding to the absorbance ratio obtained for each sample.

7.3 Determine iodide concentration in milligrams per liter as follows:

$$I^{-1} \text{ (mg/L)} = \frac{1,000}{\text{mL sample}} \times \text{mg I}^{-1}$$

## 8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

## 9. Precision

Precision expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
3	0.023	91
3	.034	91
3	.117	55

## Reference

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77-83.

# Iodide, colorimetric, ceric-arsenious oxidation, automated-segmented flow

## Parameter and Code:

Iodide, dissolved, I-2371-85 (mg/L as I): 71865

### 1. Application

This method may be used to determine iodide in fresh water and brines containing from 0.001 to 0.060 mg/L of iodide. Greater concentrations need to be reduced by dilution; however, samples containing concentrations greater than 1 mg/L need to be analyzed by the bromine oxidation method (method I-1370).

### 2. Summary of method

The method is based on the catalytic effect of iodide on the ceric-arsenious oxidation reaction in acid solution. In the presence of a small amount of iodide, the reaction follows first-order reaction-rate kinetics—and at a given temperature and for a given reaction time, the extent of reduction of ceric ion is directly proportional to the iodide concentration. Photometric measurement of the absorbance of the solution permits evaluation of the extent of the reaction (Mitchell, 1966).

### 3. Interferences

3.1 Most substances normally present in natural water do not interfere.

3.2 Bromide ion does not interfere.

3.3 Low iodide values will be obtained if the pH of the water samples is less than 3 or if the iron concentration exceeds 500  $\mu\text{g/L}$ .

### 4. Apparatus

4.1 *Technicon AutoAnalyzer II*, consisting of a sampler, proportioning pump, cartridge manifold, colorimeter, voltage stabilizer, recorder, printer, and heating bath.

4.2 With this equipment the following operating conditions have been found satisfactory for the range from 0.001 to 0.060 mg/L:

Absorption cell ----- 15 mm  
Wavelength ----- 410 nm  
Cam ----- 30/h (2/1)

### 5. Reagents

5.1 *Arsenious acid solution*, 2.782 g/L: Add 2.782 g primary standard  $\text{As}_2\text{O}_3$  to approx 500 mL demineralized water in a 1,000-mL volumetric flask. Slowly add 3 mL concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84). Warm the mixture until the  $\text{As}_2\text{O}_3$  is dissolved. Cool and dilute to 1,000 mL with demineralized water. Add a small piece of metallic arsenic to stabilize the solution.

5.2 *Ceric sulfate solution*, 1.584 g/L: Add 600 mL 2.5M  $\text{H}_2\text{SO}_4$  and 1.584 g anhydrous  $\text{Ce}(\text{HSO}_4)_4$  to a 1,000-mL volumetric flask. Warm the mixture and stir occasionally until a clear solution is obtained. Cool and dilute to volume with 2.5M  $\text{H}_2\text{SO}_4$ .

5.3 *Iodide standard solution I*, 1.00 mL = 0.100 mg  $\text{I}^{-1}$ : Dissolve 0.1308 g KI crystals, dried overnight in a sulfuric acid desiccator, in demineralized water and dilute to 1,000 mL.

5.4 *Iodide standard solution II*, 1.00 mL = 0.010 mg  $\text{I}^{-1}$ : Dilute 100 mL iodide standard solution I to 1,000 mL with demineralized water.

5.5 *Iodide standard solution III*, 1.00 mL = 0.0005 mg  $\text{I}^{-1}$ : Dilute 50.0 mL iodide standard solution II to 1,000 mL with demineralized water.

5.6 *Iodide working standards*: Prepare a blank and 500 mL each of a series of iodide working standards by appropriate quantitative dilution of the iodide standard solution III as follows:

Iodide standard solution III (mL)	Iodide concentration (mg/L)
0.0	0.000
2.0	.002
5.0	.005
10.0	.010
20.0	.020
40.0	.040
60.0	.060

5.6 *Sulfuric acid, 2.5M:* Cautiously add 139 mL concentrated  $H_2SO_4$  (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

## 6. Procedure

6.1 Set up manifold (fig. 27).

6.2 Allow colorimeter and recorder to warm up for at least 30 min.

6.3 Adjust the baseline to read zero scale division on the recorder with all reagents, but with demineralized water in the sample tube.

6.4 Place a complete set of standards and a blank in the first positions of the first sample tray, beginning with the most concentrated standard. Place individual standards of differing concentrations in approximately every eighth position of the remainder of this and subsequent sample trays. Fill remainder of each tray with samples.

6.5 Begin analysis. When the peak from the most concentrated working standard appears

on the recorder, adjust the STD CAL control until the flat portion of the peak reads full scale.

## 7. Calculations

7.1 Prepare an analytical curve by plotting the height of each peak versus its respective iodide concentration.

7.2 Compute the iodide concentration of each sample by comparing its peak height to the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

## 8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 0.1 mg/L, three decimals; 0.1 mg/L and above, two significant figures.

## 9. Precision

Precision data are not available for this method.

## Reference

Mitchell, C. G., 1966, Semimicroanalytical method for the determination of iodide in water: U.S. Geological Survey Water-Supply Paper 1822, p. 77-83.

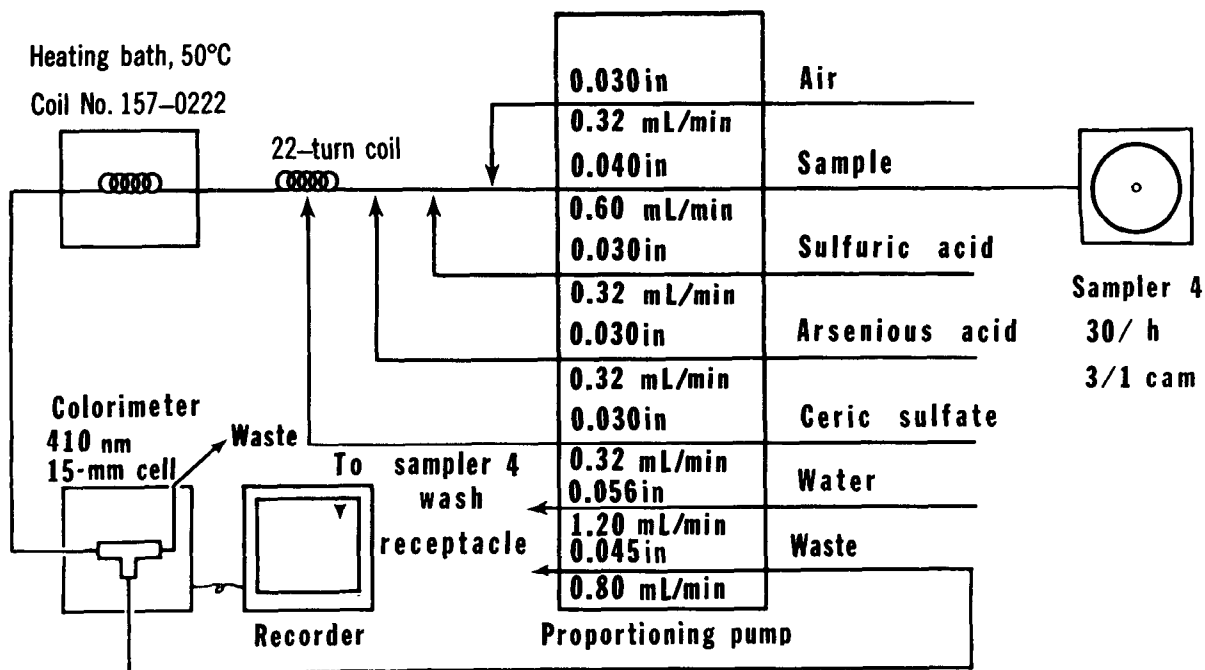


Figure 27.—Iodide, ceric-arsenious oxidation manifold

# Iodide, titrimetric, bromine oxidation

## Parameter and Code:

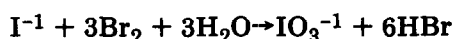
Iodide, dissolved I-1370-85 (mg/L as I): 71865

### 1. Application

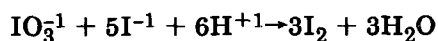
This method may be used to analyze any natural or treated water or brine containing at least 1.0 mg/L of iodide, from which interfering substances have been removed.

### 2. Summary of method

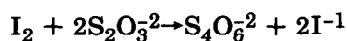
Iodide in a buffered solution is oxidized by bromine to iodate; the excess bromine is subsequently removed by adding sodium formate (Kolthoff and others, 1969):



Iodine equivalent to the iodate is then liberated by addition of potassium iodide to an acid solution:



Finally the liberated iodine is titrated with standard thiosulfate solution with starch used as the indicator:



### 3. Interferences

Iron, manganese, and organic material interfere with the basic reactions of the method, but their interferences are removed by preliminary treatment with calcium oxide.

### 4. Apparatus

- 4.1 *Buret*, 10-mL capacity.
- 4.2 *Flasks*, 250-mL capacity.

### 5. Reagents

5.1 *Acetic acid, 2.2M*: Mix 125 mL glacial  $\text{CH}_3\text{COOH}$  (sp gr 1.06) with demineralized water and dilute to 1 L.

5.2 *Bromine water, saturated*: Add to approx 250 mL demineralized water slightly more liquid  $\text{Br}_2$  than will dissolve when mixed. Store in a glass-stoppered, actinic-glass bottle.

5.3 *Calcium oxide, CaO*, anhydrous powder.

5.4 *Methyl red indicator solution*, 0.01 g/100 mL: Dissolve 0.01 g water-soluble methyl red in 100 mL demineralized water.

5.5 *Potassium fluoride, KF·2H<sub>2</sub>O*, crystals.

5.6 *Potassium iodide*, crystals,  $\text{IO}_3^{-1}$ -free: The KI can be tested for  $\text{IO}_3^{-1}$  by dissolving 0.1 g in 5 mL water, acidifying with 1 or 2 drops concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84), and adding 2 or 3 mL starch indicator. Immediate appearance of a blue color indicates the presence of  $\text{IO}_3^{-1}$ ; slow color formation is due to atmospheric oxidation.

5.7 *Sodium acetate solution*, 165 g/L: Dissolve 274 g  $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$  in demineralized water and dilute to 1 L.

5.8 *Sodium formate solution*, 50 g/100 mL: Dissolve 50 g  $\text{HCOONa}$  in hot demineralized water and dilute to 100 mL. Prepare fresh daily.

5.9 *Sodium thiosulfate solution*, 0.10N: Dissolve 25 g  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in carbon dioxide-free demineralized water. Add 1 g  $\text{Na}_2\text{CO}_3$  and dilute to 1 L.

5.10 *Sodium thiosulfate standard solution*, 0.010N: Dilute 100 mL 0.10N  $\text{Na}_2\text{S}_2\text{O}_3$  solution to 950 mL with carbon dioxide-free demineralized water and standardize against  $\text{KIO}_3$  as follows: Dry approx 0.5 g  $\text{KIO}_3$  for 2 h at 180°C. Cool and dissolve 0.3567 g in demineralized water; dilute to 1,000 mL. Pipet 25.0 mL of the  $\text{KIO}_3$  solution into a 250 mL flask; then add successively 75 mL demineralized water and 0.5 g KI crystals. After solution is complete, add 10 mL 3.6M  $\text{H}_2\text{SO}_4$ . Allow the stoppered flask to stand 5 min in the dark, then titrate with

standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color).

$$\text{Normality of Na}_2\text{S}_2\text{O}_3 = \frac{0.25}{\text{mL Na}_2\text{S}_2\text{O}_3}$$

5.11 *Starch indicator solution*, stable or "thyodene," powdered (Fisher No. T138 or equivalent).

5.12 *Sulfuric acid, 3.6M*: *Cautiously* add 200 mL concentrated  $\text{H}_2\text{SO}_4$  (sp gr 1.84) to demineralized water, cool, and dilute to 1 L.

## 6. Procedure

6.1 Remove soluble iron, manganese, and organic matter by adding a slight excess of CaO to approx 400 mL of sample; shake, let stand approx 1 h, and filter through a dry, moderately retentive filter paper. Discard the first 75 mL of filtrate.

6.2 Pipet a volume of the filtrate containing less than 5.0 mg  $\text{I}^-$  (100.0 mL max) into a 250-mL flask, and adjust the volume to 100 mL.

6.3 Prepare a blank of 100 mL demineralized water and carry it through the procedure along with the sample.

6.4 Add 1 drop methyl red indicator solution and make the solution just acid with 3.6M  $\text{H}_2\text{SO}_4$ .

6.5 Add 15.0 mL  $\text{CH}_3\text{COONa}$  solution and 5.0 mL 2.2M  $\text{CH}_3\text{COOH}$ .

6.6 Add sufficient  $\text{Br}_2$  water to produce a light-yellow color, mix, and allow to stand 5 min.

6.7 Reduce the excess  $\text{Br}_2$  by adding  $\text{HCOONa}$  solution until the yellow tinge in the sample disappears; then add 1 mL excess.

6.8 Wash the sides of the flask with a small amount of water, and expel  $\text{Br}_2$  vapors with a syringe and a glass tube inserted through the mouth of the flask.

6.9 If any iron precipitates at this point, add 0.5 g  $\text{KF} \cdot 2\text{H}_2\text{O}$ .

6.10 Add approx 1 g KI and 10 mL 3.6M  $\text{H}_2\text{SO}_4$ ; mix and let stand 5 min in the dark.

6.11 Titrate the liberated  $\text{I}_2$  with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution, adding 2 to 3 mL starch indicator solution as the end point is approached (light-straw color). Disregard a return of the blue color after the end point has been reached.

## 7. Calculations

$$\text{I}^-, \text{mg/L} = \frac{1,000}{\text{mL sample}} \times 21.15 \times$$

$$[(\text{mL titrant} - \text{mL blank}) \times N]$$

where

$N$  = normality of standard thiosulfate solution,

and

21.15 = equivalent weight of iodide.

## 8. Report

Report iodide, dissolved (71865), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

## 9. Precision

Single-operator precision of this method (American Society for Testing and Materials, 1984) may be expressed as follows:

$$S_o = 0.009X$$

where

$S_o$  = single-operator precision, milligrams per liter,

and

$X$  = concentration of iodide, milligrams per liter.

## References

- American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 476-84.
- Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, *Quantitative Chemical Analysis* (4th ed.): New York, Macmillan, 1199 p.

# Iron, atomic absorption spectrometric, direct

## Parameters and Codes:

Iron, dissolved, I-1381-85 ( $\mu\text{g/L}$  as Fe): 01046  
Iron, total recoverable, I-3381-85 ( $\mu\text{g/L}$  as Fe): 01045  
Iron, suspended recoverable, I-7381-85 ( $\mu\text{g/L}$  as Fe): 01044  
Iron, recoverable-from-bottom-material, dry wt I-5381-85 ( $\mu\text{g/g}$  as Fe): 01170

## 1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least  $10 \mu\text{g/L}$  of iron. Sample solutions containing more than  $1,000 \mu\text{g/L}$  need either to be diluted or to be read on a less expanded scale.

1.2 Suspended recoverable iron is calculated by subtracting dissolved iron from total recoverable iron.

1.3 This method may be used to analyze bottom material containing at least  $1 \mu\text{g/g}$  of iron. Prepared sample solutions containing more than  $1,000 \mu\text{g/L}$  need either to be diluted or to be read on a less expanded scale.

1.4 Total recoverable iron in water-suspended sediment needs to undergo preliminary digestion-solubilization by method I-3485, and recoverable iron in bottom material needs to undergo preliminary digestion-solubilization by method I-5485 before being determined.

## 2. Summary of method

2.1 Iron is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame.

2.2 The procedure may be automated by the addition of a sampler and either a strip-chart recorder or a printer or both.

## 3. Interferences

Individual concentrations of sodium, potassium, chloride, and sulfate ( $5,000 \text{ mg/L}$  each), calcium and magnesium ( $1,000 \text{ mg/L}$  each), nitrate ( $100 \text{ mg/L}$ ), chromium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead, lithium, mercury, selenium, aluminum,

antimony, arsenic, vanadium, boron, and molybdenum ( $1 \times 10^5 \mu\text{g/L}$  each) do not interfere. Greater concentrations of each constituent were not investigated.

## 4. Apparatus

4.1 *Atomic absorption spectrometer* equipped with electronic digital readout and automatic zero and concentration controls.

4.2 Refer to the manufacturer's manual to optimize instrument for the following:

Grating ----- Ultraviolet

Wavelength -----  $248.3 \text{ nm}$

Source (hollow-cathode

lamp) ----- Iron

Oxidant ----- Air

Fuel ----- Acetylene

Type of flame ----- Oxidizing

4.3 Different burners may be used according to manufacturers' instructions.

## 5. Reagents

5.1 *Iron standard solution I*,  $1.00 \text{ mL} = 400 \mu\text{g Fe}$ : Weigh  $0.400 \text{ g}$  analytical grade Fe wire that has been cleaned in dilute HCl, rinsed, and dried. Dissolve in  $5 \text{ mL}$  concentrated  $\text{HNO}_3$  (sp gr 1.41), warming if necessary, and dilute to  $1,000 \text{ mL}$  with demineralized water.

5.2 *Iron standard solution II*,  $1.00 \text{ mL} = 4.00 \mu\text{g Fe}$ : Dilute  $10.0 \text{ mL}$  iron standard solution I and  $1 \text{ mL}$  concentrated  $\text{HNO}_3$  (sp gr 1.41) to  $1,000 \text{ mL}$  with demineralized water. This standard is used to prepare working standards at time of analysis.

5.3 *Iron working standards*: Prepare a series of at least six working standards containing



from 10 to 1,000  $\mu\text{g/L}$  of iron by appropriate dilution of iron standard solution II with acidified water. Prepare fresh daily.

5.4 *Water, acidified:* Add 1.5 mL concentrated  $\text{HNO}_3$  (sp gr 1.41) to 1 liter of demineralized water.

## 6. Procedure

Aspirate the blank (acidified water) to set the automatic zero control. Use the automatic concentration control to set the concentrations of standards. Use at least six standards. Calibrate the instrument each time a set of samples is analyzed and check calibration at reasonable intervals.

## 7. Calculations

7.1 Determine the micrograms per liter of dissolved or total recoverable iron in each sample solution from the digital display or printer while aspirating each sample. Dilute those samples containing iron concentrations that exceed the working range of the method and multiply by the proper dilution factors.

7.2 To determine micrograms per liter suspended recoverable iron, subtract dissolved-iron concentration from total-recoverable-iron concentration.

7.3 To determine micrograms per gram of iron in bottom-material samples, first determine the micrograms per liter of iron as in paragraph 7.1; then

$$\text{Fe } (\mu\text{g/g}) = \frac{\mu\text{g/L Fe} \times \frac{\text{mL of original digest}}{1,000}}{\text{wt of sample (g)}}$$

## 8. Report

8.1 Report iron, dissolved (01046), total-recoverable (01045), and suspended-recoverable (01044), concentrations as follows: less than 100

$\mu\text{g/L}$ , nearest 10  $\mu\text{g/L}$ ; 100  $\mu\text{g/L}$  and above, two significant figures.

8.2 Report iron, recoverable-from-bottom-material (01170), concentrations as follows: less than 100  $\mu\text{g/g}$ , nearest microgram per gram; 100  $\mu\text{g/g}$  and above, two significant figures.

## 9. Precision

9.1 Precision for dissolved iron for 26 samples within the range of 38 to 996  $\mu\text{g/L}$  may be expressed as follows:

$$S_T = 0.066X + 18.58$$

where

$S_T$  = overall precision, micrograms per liter, and

$X$  = concentration of iron, micrograms per liter.

The correlation coefficient is 0.8305.

9.2 Precision for dissolved iron for six of the 26 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean ( $\mu\text{g/L}$ )	Relative standard deviation (percent)
18	38	42
29	110	25
22	277	12
16	445	10
33	750	8
13	996	6

9.3 It is estimated that the percent relative standard deviation for total recoverable and suspended recoverable iron and recoverable iron in bottom material will be greater than that reported for dissolved iron.

9.4 Precision for total recoverable iron expressed in terms of percent relative standard deviation for two water-suspended sediment mixtures is as follows:

Number of laboratories	Mean ( $\mu\text{g/L}$ )	Relative standard deviation (percent)
24	7376	49
19	7680	38

## Iron, atomic emission spectrometric, ICP

### Parameter and Code:

Iron, dissolved, I-1472-85 ( $\mu\text{g/L}$  as Fe): 01046

### 2. Summary of method

Iron is determined simultaneously with several other constituents on a single sample by a direct-reading emission spectrometric

method utilizing an induction-coupled argon plasma as an excitation source. See method I-1472, metals, atomic emission spectrometric, ICP.

## Iron, total-in-sediment, atomic absorption spectrometric, direct

### Parameters and Codes:

Iron, total, I-5473-85 (mg/kg as Fe): none assigned

Iron, total, I-5474-85 (mg/kg as Fe): none assigned

### 2. Summary of method

2.1 A sediment sample is dried, ground, and homogenized. The sample is then treated and analyzed by one of the following techniques.

2.1.1 The sample is fused with a mixture of lithium metaborate and lithium tetraborate in a graphite crucible in a muffle furnace at 1000°C. The resulting bead is dissolved in acidified, boiling, demineralized water; iron is then determined by atomic absorption spectrometry. See method

I-5473, metals, major, total-in-sediment, atomic absorption spectrometric, direct.

2.1.2 The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200°C. Iron is determined on the resulting solution by atomic absorption spectrometry. See method I-5474, metals, major and minor, total-in-sediment, atomic absorption spectrometric, direct.