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Techniques of Water-Resources Investigations
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Chapter A1

METHODS FOR DETERMINATION OF INORGANIC SUBSTANCES IN WATER AND FLUVIAL SEDIMENTS

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Book 5
LABORATORY ANALYSIS

Carbon dioxide, calculation

Parameter and Code:
Carbon dioxide, dissolved, I-1160-85 (mg/L as CO_2): 00405

1. Application

This method may be applied to any sample for which measured values of pH and bicarbonate ion are available.

2. Summary of method

2.1 Carbon dioxide concentration is calculated from measured values of pH and bicarbonate ion. The pH is determined potentiometrically (method I-1586) and the bicarbonate ion by electrometric titration (method I-1030).

2.2 Gaseous carbon dioxide hydrolyzes slightly:

$$CO_2(aq) + H_2O \rightarrow H_2CO_3 \quad (1)$$

The hydrolysis constant expression is:

$$K_{hydr} = \frac{[H_2CO_3]}{[CO_2]} = 2.6\times10^{-3} \quad (2)$$

The square brackets denote concentrations in moles per liter.

Carbonic acid is a weak acid and dissociates by steps:

$$H_2CO_3 \leftrightarrows H^{+1} + HCO_3^{-1} \quad (3)$$

$$HCO_3^{-1} \leftrightarrows H^{+1} + CO_3^{-2} \quad (4)$$

Only the two equilibria represented by equations (1) and (3), however, are usually of significance in determining CO_2 concentrations. When the pH of a water is sufficiently high to permit the existence of CO_3^{-2}, the concentration of free CO_2 that can coexist is negligibly small.

The CO_2 concentrations can, therefore, be calculated within experimental accuracy from equations (1) and (3) and their corresponding equilibrium-constant expressions as follows:

$$K_{hydr} = \frac{[H_2CO_3]}{[CO_2]} = 2.6\times10^{-3} \quad (5)$$

$$K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[H_2CO_3]} = 1.7\times10^{-4} \quad (6)$$

Multiply equations (5) and (6):

$$K_{hydr}\,K_1 = \frac{[H^{+1}]\,[HCO_3^{-1}]}{[CO_2]} = 4.4\times10^{-7} \quad (7)$$

and solving for $[CO_2]$:

$$[CO_2] = \frac{[H^{+1}]\,[HCO_3^{-1}]}{4.4\times10^{-7}} \quad (2)$$

This equation can then be used to determine the CO_2 concentration when $[HCO_3^{-1}]$ and $[H^{+1}]$, or pH, of the sample have been determined. Equation (8) can be rearranged to simplify the calculation, since both CO_2 and bicarbonate $[HCO_3^{-1}]$ concentrations are usually expressed in units of milligrams per liter rather than of moles per liter, and hydrogen-ion concentrations normally as pH units:

$$\text{mg } CO_2/L = 1.60\times10^{(6.0-pH)}\times\text{mg } HCO_3^{-1}/L \quad (9)$$

For convenience in making the calculations, the values of $1.60\times10^{(6.0-pH)}$ may be tabulated for a range of pH values (table 7).

2.3 For additional information on the theory of this method see De Martini (1938), Langelier

Table 7.—Values of $1.60 \times 10^{(6.0-pH)}$

pH	$1.60 \times 10^{(6.0-pH)}$	pH	$1.60 \times 10^{(6.0-pH)}$
6.0	1.60	7.6	0.040
6.2	1.00	7.8	.025
6.4	.633	8.0	.016
6.6	.399	8.2	.010
6.8	.252	8.4	.006
7.0	.160	8.6	.004
7.2	.100	8.8	.003
7.4	.063	9.0	.002

(1936), Larson and Buswell (1942), and Moore (1939).

3. Interferences

3.1 The values of the constants K_{hydr} and K_1 vary with temperature and with both the concentration and nature of the dissolved solutes. Therefore, the accuracy of the calculation depends on the reliability of values of K_{hydr} and K_1 for a particular sample. For practical purposes and for most samples containing less than 800 mg/L of solutes, a value for $(K_{hydr} \times K_1)$ of 4.54×10^{-7} has been recommended and was used in calculating the constant factor of equation (9).

3.2 Carbon dioxide is easily lost from solution, and precautions must be taken to prevent or minimize such losses when collecting the sample. The pH and bicarbonate must be determined in the field at the time of collection.

7. Calculations

7.1 Calculate mg/L CO_2 as follows:

$$\text{mg/L } CO_2 = 1.60 \times 10^{(6.0-pH)} \times \text{mg/L } HCO_3^{-1}$$

7.2 The calculated values of the variable $1.60 \times 10^{(6.0-pH)}$ are shown in table 7.

8. Report

Report carbon dioxide, dissolved, calculation (00405), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision data are not available for this method.

References

De Martini, F. E., 1938, Corrosion and the Langelier calcium carbonate saturation index: American Water Works Association Journal v. 30, p. 85.

Langelier, W. F., 1936, The analytical control of anti-corrosion water treatment: American Water Works Association Journal, v. 28 p. 1500.

Larson, T. E., and Buswell, A. N., 1942, Calcium carbonate saturation and alkalinity interpretations: American Water Works Association Journal, v. 34, p. 1667.

Moore, E. W., 1939, Graphic determination of carbon dioxide and three forms of alkalinity: American Water Works Association Journal, v. 31, p. 51.

Chloride, colorimetric, ferric thiocyanate

Parameter and Code:

Chloride, dissolved, I-1187-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine dissolved chloride in water containing from 0.1 to 10 mg/L of chloride ion. It is particularly useful for the analysis of low-dissolved- solids-content water when low chloride concentrations must be determined accurately.

2. Summary of method

2.1 Chloride is determined by measurement of the color developed by the displacement of the thiocyanate ion from mercuric thiocyanate by chloride ion in the presence of ferric ion; an intensely colored ferric thiocyanate complex is formed:

$$2Cl^{-1} + Hg(SCN)_2 + 2Fe^{+3} \rightarrow HgCl_2 + 2Fe(SCN)^{+2}$$

2.2 The color is stable for at least 2 h and is proportional to the chloride-ion concentration. The color has a maximum absorbance at 460 nm.

2.3 For additional information see ASTM Method D 512-81, "Standard Methods of Testing for Chloride Ion in Water" (American Society for Testing and Materials, 1984).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Spectrometer* for use at 460 nm.

4.2 Refer to manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180 °C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride standard solution II*, 1.00 mL= 0.010 mg Cl^{-1}: Dilute 5.0 mL chloride standard solution I to 500.0 mL with demineralized water.

5.3 *Ferric ammonium sulfate solution*, 22.8 g/L: Dissolve 41.4 g $FeNH_4(SO_4)_2 \cdot 12H_2O$ in 570 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L with demineralized water.

5.4 *Mercuric thiocyanate solution*, 3 g/L: Dissolve 3 g $Hg(SCN)_2$ in 1 L 95-percent ethanol (denatured alcohol formula No. 3A is also satisfactory). Stir for 1 h to saturate the solvent; allow undissolved thiocyanate to settle, and then filter through a Pyrex-wool plug or a 0.45-μm membrane filter.

6. Procedure

6.1 Pipet a volume of sample containing less than 0.250 mg of Cl^{-1} (25.0 mL max) into a 50-mL beaker and adjust the volume to 25.0 mL with demineralized water.

6.2 Prepare a demineralized-water blank and at least five standards containing from 0.0025 to 0.250 mg Cl^{-1}, and adjust the volume of each to 25.0 mL.

6.3 Add 2.0 mL $FeNH_4(SO_4)_2$ solution and stir. The samples will be essentially colorless at this point.

6.4 Add 2.0 mL $Hg(SCN)_2$ solution and stir.

6.5 After at least 10 min, but within 2 h, read the absorbance of each standard and sample against the blank at 460 nm, and, when necessary, make corrections for water color.

7. Calculations

7.1 Determine the milligrams chloride from a plot of absorbances of standards containing known amounts of Cl^{-1}.

7.2 Determine the chloride concentration in milligrams per liter as follows:

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

8. Report

Report chloride, dissolved (00940), concentrations of less than 10 mg/L to the nearest 0.1 mg/L.

9. Precision

9.1 Data published by the American Society for Testing and Materials (1984) indicate the overall precision of the method to be

$$S_T = 0.054X$$

where

S_T=overall precision, milligrams per liter, and

X=concentration of Cl^{-1}, milligrams per liter.

9.2 Precision for one reference sample expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
6	1.4	33

Reference

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 392-400.

Chloride, colorimetric, ferric thiocyanate, automated-segmented flow

Parameter and Code:

Chloride, dissolved, I-2187-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine concentrations of chloride in surface, domestic, and industrial water in the range of 10 to 100 mg/L or 0.1 to 10.0 mg/L. The latter range can be attained by interchanging the sample and diluent pump tubes.

2. Summary of method

This method is based on the displacement of thiocyanate from mercuric thiocyanate by chloride and on the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the intensely colored ferric thiocyanate complex. The absorbance of this complex is then measured colorimetrically (O'Brien, 1962; Zall and others, 1956).

$$Hg(SCN)_2 + 2Cl^{-1} \rightarrow HgCl_2 + 2SCN^{-1}$$

$$SCN^{-1} + Fe^{+3} \rightarrow Fe(SCN)^{+2}$$

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

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

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 10 to 100 mg/L and from 0.1 to 10.0 mg/L:

Absorption cell -----	15 mm
Wavelength --------	480 nm
Cam ----------	60/h (6/1)

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 0.50 mg Cl^{-1}: Dissolve 0.8242 g primary standard NaCl crystals, dried at 180° C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride working standards*; Prepare a blank and 500 mL each of a series of chloride working standards by appropriate quantitative dilution of the chloride standard solution I, as follows:

Chloride standard solution (mL)	Chloride concentration (mg/L)
0.0	0.0
5.0	5.0
10.0	10.0
20.0	20.0
30.0	30.0
50.0	50.0
60.0	60.0
80.0	80.0
100.0	100.0

5.3 *Ferric nitrate stock solution*, 121 g/L: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in approx 500 mL demineralized water. Add 225 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L. Filter and store in an amber-colored container.

5.4 *Mercuric thiocyanate stock solution*, 4.17 g/L in methanol: Dissolve 4.17 g $Hg(SCN)_2$ in 500 mL methanol, dilute to 1 L with methanol, and filter.

5.5 *Chloride color reagent*: Add 150 mL ferric nitrate stock solution and 150 mL mercuric thiocyanate stock solution to demineralized water and dilute to 1 L. Add 1 mL/L of Brij-35 solution. Use amber bottle for storage.

6. Procedure

6.1 Set up manifold (fig. 20).

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

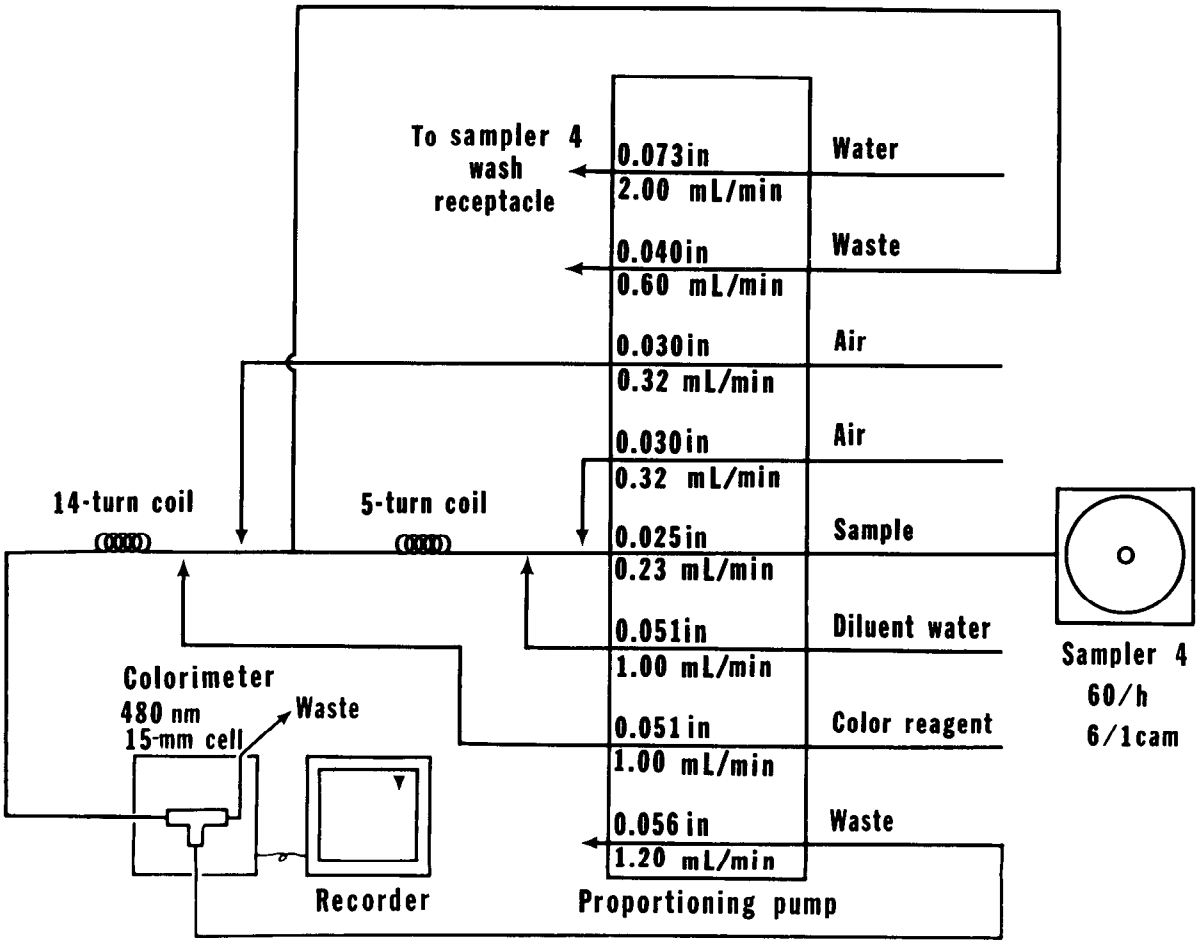

Figure 20.—Chloride, ferric thiocyanate manifold

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

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 unknown samples. (NOTE 1).

NOTE 1. The sample cups should remain sealed in their packages until just prior to use to avoid contamination. Handle cups carefully to avoid contamination from perspiration on hands.

6.5 Begin analysis. When the peak from 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 standard peak versus its respective chloride concentration.

7.2 Compute the chloride-ion 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 chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 20 samples within the range of 0.3 to 246 mg/L may be expressed as follows:

$$S_T = 0.027X + 0.786$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8935.

9.2 Precision for six of the 20 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.31	81
16	1.50	33
19	25.7	3
9	58.8	3
6	122	6
12	246	3

References

O'Brien, J. E., 1962, Automatic analysis of chlorides in sewage: Wastes Engineering, v. 33, p. 670–672.

Zall, D. M., Fisher, D., and Garner, M. Q., 1956, Photometric determination of chlorides in water: Analytical Chemistry, v. 28 p. 1665–1668.

Chloride, colorimetric, ferric thiocyanate, automated-discrete

Parameter and Code:

Chloride, dissolved, I-2188-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine concentrations of chloride in surface, domestic, and industrial water in the ranges of 0.1 to 10.0 mg/L and 10.0 to 500 mg/L. Samples containing greater concentrations need to be diluted.

2. Summary of method

2.1 This method is based on the displacement of thiocyanate from mercuric thiocyanate by chloride and on the subsequent reaction of the liberated thiocyanate ion with ferric ion to form the intensely colored ferric thiocyanate complex. The absorbance of this complex is then measured colorimetrically (O'Brien, 1962; Zall and others, 1956).

$$Hg(SCN)_2 + 2Cl^{-1} \rightarrow HgCl_2 + 2SCN^{-1}$$

$$SCN^{-1} + Fe^{+3} \rightarrow Fe(SCN)^{+2}$$

2.2 For additional information see ASTM Method D512-81, "Standard Methods of Test for Chloride Ion in Water" (American Society for Testing and Materials, 1984).

3. Interferences

Bromide, iodide, cyanide, thiosulfate, and nitrite interfere. Color, depending upon its spectral absorbance, may interfere with the photometric measurement.

4. Apparatus

4.1 *Discrete analyzer system*, American Monitor IQAS or equivalent.

4.2 With this equipment the following operating conditions have been found satisfactory for the ranges from 0.1 to 10.0 mg/L and from 10.0 to 500 mg/L.

Wavelength -----	480 nm
Absorption cell --	1 cm_2, flow-through, temperature-controlled
Reaction temperature --------	37 °C or ambient
Sample volumes -	0.35 mL with 0.050 mL of diluent for 0.1 to 10.0 mg/L and 0.035 mL with 0.065 mL of diluent for 10.0 to 500 mg/L
Reagent volumes	0.90 mL color reagent for 0.1 to 10.0 mg/L and 1.4 mL color reagent for 10.0 to 500 mg/L (NOTE 1)

NOTE 1. Sample-to-diluent ratio and reagent volumes must be optimized for each instrument according to manufacturer's specifications.

5. Reagents

5.1 *Chloride standard solution I*, 1.00 mL= 10.00 mg Cl^{-1}: Dissolve 16.485 g primary standard NaCl crystals, dried at 180 °C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Chloride standard solution II*, 1.00 mL= 0.10 mg Cl^{-1}: Dilute 10.0 mL chloride standard solution I to 1,000 mL with demineralized water.

5.3 *Chloride working standards*, low range: Prepare a blank and 1,000 mL each of a series of chloride working standards by appropriate dilution of the chloride standard solution II as follows:

Chloride standard solution II (mL)	Chloride concentration (mg/L)
0.0	0.00
1.00	.10
5.00	.50
10.0	1.00
50.0	5.00
100.0	10.00

5.4 *Chloride working standards*, high-range: Prepare 1,000 mL each of a series of chloride working standards by appropriate dilution of the chloride standard solution I, as follows:

Chloride standard solution II (mL)	Chloride concentration (mg/L)
4.0	40
8.0	80
30.0	300
50.0	500

5.5 *Ferric nitrate stock solution*, 121 g/L: Dissolve 202 g $Fe(NO_3)_3 \cdot 9H_2O$ in approx 500 mL demineralized water. Add 225 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1 L. Filter and store in an amber-colored container.

5.6 *Mercuric thiocyanate stock solution*, saturated: Add approx 5 g $Hg(SCN)_2$ to 1 L methanol. Mix thoroughly for 0.5 h and let stand. Remove excess $Hg(SCN)_2$ by filtration. **CAUTION—Poisonous.**

5.7 *Chloride color reagent*: Add 150 mL ferric nitrate stock solution and 150 mL mercuric thiocyanate stock solution to demineralized water and dilute to 1 L. Store in amber bottle. Prepare fresh daily.

6. Procedure

6.1 Set up analyzer and computer-card assignments according to manufacturer's instructions.

6.2 Place five standards and a blank, beginning with the lowest concentration, in the first positions on the sample turntable. For the low range use 0.10, 0.50, 1.00, 5.00, and 10.0 mg/L, and for the high range use 10, 40, 80, 300, and 500 mg/L. Fill remainder of turntable with samples.

6.3 Begin analysis. Printer will acknowledge parameter and concentration range selected, listing each sample-cup number and corresponding concentration. During each run the cathode-ray tube (CRT) display will identify a plot of standards and samples, and list blank and reagent optical densities with slope calculations.

7. Calculations

Obtain the milligrams per liter of chloride in each sample from the printer.

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

Precision expressed in terms of the standard deviation and percent relative standard deviation for replicate analysis by a single operator is as follows:

Mean (mg/L)	Std. Deviation (mg/L)	Relative standard deviation (percent)
0.38	0.06	16
5.72	.07	1.2
15.0	.08	.5
21.4	1.0	4.7
177	1.3	.7

References

American Society for Testing and Materials, 1984, Annual book of ASTM Standards, section 11, water: Philadelphia, v. 11.01, p. 392-400.

O'Brien, J. E., 1962, Automatic analysis of chlorides in sewage: Wastes Engineering, v. 33, p. 670-672.

Zall, D. M., Fisher, D., and Garner, M. Q., 1956, Photometric determination of chlorides in water: Analytical Chemistry, v. 28, p. 1665-1668.

Chloride, titrimetric, mercurimetric

Parameter and Code:
Chloride, dissolved, I-1184-85 (mg/L as Cl): 00940

1. Application

This method may be used to determine chloride in water containing at least 0.1 mg/L of chloride. Samples containing lower concentrations need to be concentrated by evaporation.

2. Summary of method

2.1 Mercuric and chloride ions form a highly stable, soluble complex.

$$Hg^{+2} + 2Cl^{-1} \rightleftarrows HgCl_2$$

Thus, the chloride in a sample may be titrated with a standard solution of a soluble mercuric salt such as mercuric nitrate. The equivalence point is detected by adding a small amount of diphenylcarbazone to the sample. A slight excess of mercuric ions, above that required to complex all of the chloride, reacts with this indicator to form a blue-violet complex (Dubsky and Trtilek, 1933, 1934; Clarke, 1950).

2.2 The optimum pH range for the titration is between 3.0 and 3.6. If the titration is made in a solution whose pH is less than 3.0, the results will be high, and if in a solution of pH greater than 3.6, the results will be low (Clarke, 1950; Thomas, 1954). The proper pH for the titration is easily obtained by adding bromophenol blue indicator and carefully adding dilute nitric acid or sodium hydroxide to adjust the sample to the desired pH.

2.3 Two standard mercuric nitrate solutions are required. A dilute solution should be used to titrate samples containing less than 200 mg/L chloride; a more concentrated mercuric nitrate solution should be used to titrate samples containing more than 200 mg/L.

3. Interferences

The method is not subject to interference from any of the anions and cations normally found in natural waters; as much as 1,000 mg/L of nitrate, sulfate, phosphate, magnesium, and calcium and 1×10^6 µg/L of aluminum do not interfere. One thousand µg/L of zinc, lead, nickel, ferrous, and chromous ions affect the colors of the solution, but not the accuracy of the titration. Nickel ion at a concentration of 1×10^5 µg/L is purple in neutral solution, green in acid solution, but gray at the chloride end point. Copper ion is tolerable up to 50,000 µg/L. Chromate and ferric ions, if present at concentrations exceeding 10,000 µg/L, must be reduced to their lower valence state prior to titration. The addition of dilute fresh hydroquinone solution insures reduction of these ions. Sulfite ion interferes at concentrations above 10 mg/L; the addition of a small amount of 30-percent hydrogen peroxide eliminates sulfite interference. Bromide and iodide are titrated with the chloride.

4. Apparatus

4.1 *Buret*, 5-, 10-, or 25-mL capacity.

4.2 *Fluorescent lamp*, white.

4.3 *Stirrer*, magnetic.

5. Reagents

5.1 *Chloride standard solution*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180 °C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Hydrogen peroxide*, 30-percent.

5.3 *Hydroquinone solution*, 1 g/100 mL: Dissolve 1.0 g purified hydroquinone in demineralized water and dilute to 100 mL.

5.4 *Mercuric nitrate standard solution I*, 1.00 mL ≙ 1.00 mg Cl^{-1}: Dissolve 4.832 g

$Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.5 *Mercuric nitrate standard solution II*, 1.00 mL ≙ 0.500 mg Cl^{-1}: Dissolve 2.416 g $Hg(NO_3)_2 \cdot H_2O$ in 25 mL demineralized water acidified with 0.25 mL concentrated HNO_3 (sp gr 1.41) and dilute to 1,000 mL. Filter, if necessary, and standardize by titrating 10.00 mL chloride standard solution diluted to 50 mL with demineralized water.

5.6 *Mixed indicator solution*: Dissolve 0.5 g crystalline diphenylcarbazone (Eastman Kodak No. 4459) and 0.05 g bromophenol blue (Eastman Kodak No. 752) in 75 mL ethanol (methyl alcohol or specially denatured alcohol No. 3A are also suitable), and dilute to 100 mL with the alcohol. Store in a brown bottle; discard after 6 months.

5.7 *Nitric acid*, 0.05*M*: Dilute 3.0 mL concentrated HNO_3 (sp gr 1.41) to 1 L with demineralized water.

5.8 *Sodium hydroxide solution*, 0.05*M*: Dissolve 2.0 g NaOH in demineralized water and dilute to 1 L.

6. Procedure

6.1 Pipet a volume of sample containing less than 20 mg Cl^{-1} (50.0 mL max) into a 125-mL Erlenmeyer flask, and adjust the volume to approx 50 mL. If the sample contains less than 0.1 mg/L of Cl^{-1}, evaporate an appropriate volume to 50 mL.

6.2 Place the flask on a magnetic stirrer and add 10 drops mixed indicator solution.

6.3 If a blue, blue-violet, or red color develops, add 0.05*M* HNO_3 by drops until the color changes to yellow. Add 1.0 mL excess acid. If a yellow or orange color forms when the mixed indicator is added, add 0.05*M* NaOH solution by drops until the color changes to blue violet; then add 0.05*M* HNO_3 by drops until the color changes to yellow; then add 1 mL excess.

6.4 Titrate the solution with mercuric nitrate standard solution I or II until a blue-violet color persists throughout the solution.

6.5 Determine a blank correction by similarly titrating 50 mL demineralized water.

6.6 Alternatively, the end point of the titration may be determined spectrophotometrically, with attendant improvement in precision. Refer to specific manufacturer's manual for details. Reagents are identical to those specified for the visual determination using the mercurimetric method.

7. Calculations

$$Cl^{-1}\ (mg/L) = \frac{1{,}000}{mL\ sample} \times (mL\ titrant - mL\ blank) \times (mg\ Cl\ per\ mL\ titrant)$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 36 samples within the range of 0.29 to 243 mg/L may be expressed as follows:

$$S_T = 0.045X + 0.581$$

where

S_T= overall precision, milligrams per liter,

and

X= concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8862.

9.2 Precision for seven of the 36 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
7	0.29	59
11	1.92	40
17	9.25	18
20	26.4	7
16	58.0	5
15	120	4
18	243	5

References

Clarke, F. E., 1950, Determination of chloride in water: Analytical Chemistry, v. 22, p. 553–5, 1458.

Dubsky, J. V., and Trtilek, J., 1933, Microvolumetric analysis using diphenylcarbazide and diphenylcarbazone as indicators (mercurimetry): Mikrochemie, v. 12, p. 315.

_____1934, Mercurimetric determination of iodide using diphenylcarbazone as indicator: Mikrochemie, v. 15, p. 95.

Thomas, J. F., 1954, Mercurimetric determination of chlorides: American Water Works Association Journal, v. 46, p. 257–62.

Chloride, titrimetric, Mohr

Parameter and Code:
Chloride, dissolved, I-1183-85 (mg/L as Cl): 00940

1. Application

1.1 This procedure is recommended for water containing concentrations of chloride between 10 and 2000 mg/L, although it can be used satisfactorily for measuring chloride concentrations up to 5,000 mg/L.

1.2 Two titrant solutions of different concentrations are recommended. The more dilute titrant is used when the chloride concentration is less than 200 mg/L. However, the end point is not as sharp as when a more concentrated titrant is used, and the latter is recommended when the chloride concentration of the sample exceeds 200 mg/L. In high-chloride waters, the voluminous precipitate tends to mask the end point, and the maximum amount of chloride that can be titrated satisfactorily is about 50 mg. Excessive sample dilution decreases both the precision and accuracy of the determination. Sample aliquots of less than 10 mL are not recommended.

2. Summary of method

2.1 In the well-known Mohr method for determination of chloride, the solution is saturated with silver chloride at the equivalence point and contains equal concentrations of silver and chloride ions. When potassium chromate is used as an indicator, a slight excess of silver precipitates as red-silver chromate. The following reactions occur:

$$Ag^{+1} + Cl^{-1} \rightarrow AgCl$$

$$2Ag^{+1} + CrO_4^{-2} \rightarrow Ag_2CrO_4$$

The pH for the titration should be between 7.0 and 10.5. In an acid medium, the sensitivity of the method is decreased; the second ionization constant of chromic acid is small, and, therefore, the chromate ion reacts with hydrogen ions.

$$CrO_4^{-2} + H^{+1} \leftrightharpoons HCrO_4^{-1}$$

The solution should not be too alkaline because of the limited solubility of silver hydroxide (Collins, 1928). Calcium carbonate can be used to adjust the pH of acidic waters without danger of making the solution too alkaline. Detection of the end point is facilitated by illuminating the titration with yellow light or by viewing the titration through yellow goggles or a filter.

2.2 Additional information on the principle of the determination is given by Kolthoff and others (1969).

3. Interferences

Iodide and bromide titrate stoichiometrically as chloride. Phosphate, sulfide, and cyanide interfere. Sulfide and cyanide can be removed by acidifying and boiling the sample, and then adjusting the pH with calcium carbonate. Hydrogen sulfide can often be removed by passing pure air through the sample. Sulfite interferes but can be oxidized readily to sulfate with hydrogen peroxide.

4. Apparatus

4.1 *Buret*, 25-mL capacity.

4.2 *Yellow light* (or filter).

5. Reagents

5.1 *Chloride standard solution*, 1.00 mL= 1.00 mg Cl^{-1}: Dissolve 1.648 g primary standard NaCl crystals, dried at 180 °C for 1 h, in demineralized water and dilute to 1,000 mL.

5.2 *Potassium chromate indicator solution,* 5 g/100 mL: Dissolve 5 g K_2CrO_4 in 100 mL demineralized water. Add silver standard solution II until a small amount of red Ag_2CrO_4 precipitates. Allow to stand overnight and filter to remove the Ag_2CrO_4.

5.3 *Silver standard solution I,* 1.00 mL ≙ 5.00 mg Cl^{-1}. Pulverize approx 30 g $AgNO_3$ crystals in a clean mortar and dry at 105 to 120°C. Discoloration of the crystals indicates decomposition caused by excessive drying temperature or impurities. Dissolve 23.96 g dried $AgNO_3$ in demineralized water and dilute to 950 mL. Standardize by titrating 25.00 mL chloride standard solution diluted to 50 mL. Store in a light-proof bottle.

5.4 *Silver standard solution II,* 1.00 mL ≙ 0.50 mg Cl^{-1}: Dilute 100 mL silver standard solution I with demineralized water to 1,000 mL. Check the titer of the reagent by titrating 10.00 mL chloride standard solution. Store in light-proof bottle.

6. Procedure

6.1 Pipet a volume of sample containing less than 50 mg Cl^{-1} (50.00 mL max) into a porcelain evaporating dish, and adjust the volume to approx 50 mL.

6.2 Add 10 drops K_2CrO_4 indicator solution.

6.3 With constant stirring, titrate with silver standard solution I or II until the pink-red Ag_2CrO_4 persists for 10 to 15 sec.

6.4 Determine a blank correction by similarly titrating 50 mL demineralized water. The normal blank correction with silver standard solution II is 0.05 or 0.10 mL. No blank correction is required with the more concentrated titrant.

7. Calculations

$$Cl^{-1}\ (mg/L) = \frac{1{,}000}{mL\ sample} \times (mL\ titrant - mL\ blank) \times (mg\ Cl^{-1}\ per\ mL\ titrant)$$

8. Report

Report chloride, dissolved (00940), concentrations as follows: less than 10 mg/L, one decimal; 10 mg/L and above, two significant figures.

9. Precision

9.1 Precision for 37 samples within the range of 0.22 to 244 mg/L may be expressed as follows:

$$S_T = 0.036X + 0.532$$

where

S_T = overall precision, milligrams per liter, and

X = concentration of chloride, milligrams per liter.

The correlation coefficient is 0.8550.

9.2 Precision for seven of the 37 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (mg/L)	Relative standard deviation (percent)
12	0.22	100
7	.29	72
10	8.59	13
21	46.0	4
13	95.8	3
12	123	6
16	244	5

References

Collins, W. D., 1928, Notes on practical water analysis: U.S. Geological Survey Water-Supply Paper 596-H, p. 235-266.

Kolthoff, I. M., Sandell, E. B., Meehan, E. J., and Bruckenstein, S., 1969, Quantitative chemical analysis [4th ed.]: New York, MacMillan, 1199 p.

Chloride, ion-exchange chromatographic, automated

Parameters and Codes:

Chloride, dissolved, I-2057-85 (mg/L as Cl): 00940
Chloride, dissolved, I-2058-85 (mg/L as Cl): 00940

2. Summary of method

Chloride 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.

Chromium, atomic absorption spectrometric, chelation-extraction

Parameters and Codes:

Chromium, dissolved, I-1238-85 (μg/L as Cr): 01030
Chromium, total recoverable, I-3238-85 (μg/L as Cr): 01034
Chromium, suspended recoverable, I-7238-85 (μg/L as Cr): 01031

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 1 to 25 μg/L of chromium. Samples containing more than 25 μg/L need either to be diluted prior to chelation-extraction or to be analyzed by the atomic absorption spectrometric direct method.

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

1.3 Total recoverable chromium in water-suspended sediment needs to undergo a preliminary digestion-solubilization by method I-3485 before being determined.

1.4 If the iron concentration of the sample exceeds 5,000 μg/L, determine chromium by the atomic absorption spectrometric direct method.

2. Summary of method

2.1 Chromium is determined by atomic absorption spectrometry. Any trivalent chromium present is oxidized by potassium permanganate to the hexavalent state. The oxidized chromium, together with hexavalent chromium originally present, is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Midgett and Fishman, 1967).

2.2 Excess permanganate is reduced with sodium azide, which must not be present in excess because it interferes with subsequent pH adjustment and chelation.

3. Interferences

3.1 The optimum pH for the extraction of the hexavalent chromium-APDC complex by methyl isobutyl ketone (MIBK) is 3.1. At this pH, however, manganese is also partially extracted. The manganese-APDC complex is unstable and decomposes to a fine suspension of manganese oxides that clogs the atomizer-burner. If the pH of the sample is adjusted to 2.4 prior to chelation and extraction, less manganese is extracted, and there is only a slight loss in extraction efficiency for chromium. If the extract is not clear after standing overnight, it must be centrifuged.

3.2 Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

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	357.9 nm
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

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

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate solution*, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Bromophenol blue indicator solution*, 0.1

g/100 mL: Dissolve 0.1 g bromophenol blue in 100 mL 50-percent ethanol.

5.3 *Chromium standard solution I*, 1.00 mL=100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.4 *Chromium standard solution II*, 1.00 mL=2.00 μg Cr^{+3} Pipet 5.0 mL chromium standard solution I into an Erlenmeyer flask. Add approximately 15 mg Na_2SO_3 and 0.5 mL concentrated HNO_3 (sp gr 1.41). Gently evaporate just to dryness; strong heating re-oxidizes the Cr. Add 0.5 mL concentrated HNO_3 and again evaporate to dryness to destroy any excess sulfite. Dissolve the residue in 1 mL concentrated HNO_3 with warming. Cool, transfer to a 250-mL volumetric flask, and dilute to the mark with demineralized water.

5.5 *Chromium standard solution III*, 1.00 mL=0.50 μg Cr^{+3}: Dilute 25.0 mL chromium standard solution II to 100 mL with demineralized water. Prepare immediately before use.

5.6 *Methyl isobutyl ketone* (MIBK).

5.7 *Potassium permanganate solution*, 0.32 g/100 mL: Dissolve 0.32 g $KMnO_4$ in demineralized water and dilute to 100 mL. Allow to stand several days and decant if necessary.

5.8 *Sodium azide solution*, 0.10 g/100 mL: Dissolve 0.10 g NaN_3 in 100 mL demineralized water.

5.9 *Sodium hydroxide solution*, 1*M*: Dissolve 40 g NaOH in demineralized water and dilute to 1 L.

5.10 *Sulfuric acid*, 0.12*M*: *Cautiously*, add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 1 L.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1 + 9) and rinse with demineralized water immediately before use.

6.2 Pipet a volume of sample solution containing less than 2.5 μg Cr (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL. The pH must be 2.0 or less. Add concentrated HNO_3 if necessary.

6.3 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards, and adjust the volume of each to approx 100 mL with the acidified demineralized water.

6.4 Add $KMnO_4$ solution by drops to blank, standards, and samples until a faint-pink color persists.

6.5 Heat on a steam bath for 20 min. If the color disappears, add $KMnO_4$ solution by drops to maintain a slight excess.

6.6 While blanks, samples, and standards are still on the steam bath, add NaN_3 solution by drops until $KMnO_4$ color just disappears. Heat for about 2 min between each addition and avoid adding any excess. Continue heating for 5 min after adding the last drop of sodium azide solution.

6.7 Transfer to a water bath and cool to room temperature.

6.8 Remove from the water bath and filter through Whatman No. 40 filter paper any sample that has a brownish precipitate or coloration that may interfere with the pH adjustment.

6.9 Add 2.0 mL 1*M* NaOH and 2 drops bromophenol blue indicator solution. Continue the addition of 1*M* NaOH by drops to all samples and standards in which the indicator change from yellow to blue has not occurred. Add 0.12*M* H_2SO_4 by drops until the blue color just disappears; then add 2.0 mL in excess. The pH at this point should be 2.4 (NOTE 1).

NOTE 1. The pH adjustment in paragraph 6.9 may be made with a pH meter instead of with an indicator, in which case the filtration called for in paragraph 6.8 will not be necessary.

6.10 Add 5.0 mL APDC solution and shake for 3 min. The pH at this point should be 2.8.

6.11 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.12 Allow the layers to separate and then add demineralized water until the ketone layer is completely in the neck of the flask.

6.13 Stopper and allow to stand overnight. The Cr^{+6}-APDC complex is stable for at least 36 h.

6.14 Aspirate the ketone layer of the blank 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 chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factors.

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

8. Report

Report chromium, dissolved (01030), total-recoverable (01034), and suspended-recoverable (01031), concentrations as follows: less than 100 μg/L, the nearest microgram per liter; 100 μg/L and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved chromium within the range of 5.8 to 47.8 μg/L for 14 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 13.2 μg/L ranged from 11.2 to 16.1 μg/L.

9.2 Precision for dissolved chromium for seven of the 14 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
4	5.75	66
3	9.67	6
12	12.9	113
11	18.7	66
3	20.0	39
3	44.3	9
9	47.8	55

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

Reference

Midgett, M. R., and Fishman, M. J., 1967, Determination of total chromium in fresh waters by atomic absorption: Atomic Absorption Newsletter, v. 6, p. 128–131.

Chromium, atomic absorption spectrometric, direct

Parameters and Codes:

Chromium, dissolved, I-1236-85 (μg/L as Cr): 01030
Chromium, total recoverable, I-3236-85 (μg/L as Cr): 01034
Chromium, suspended recoverable, I-7236-85 (μg/L as Cr): 01031
Chromium, recoverable-from-bottom-material, I-5236-85 (μg/g as Cr): 01029

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing at least 10 μg/L of chromium. Sample solutions containing more than 400 μg/L need to be diluted. Sample solutions containing less than 10 μg/L and brines need to be analyzed by the atomic absorption spectrometric chelation-extraction method, providing that the interference limits discussed in that method are not exceeded.

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

1.3 This method may be used to analyze bottom material containing at least 1 μg/g of chromium. Sample solutions containing more than 400 μg/L need to be diluted.

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

2. Summary of method

Chromium is determined by atomic absorption spectrometry by direct aspiration of the sample solution into an air-acetylene flame. Ammonium chloride is added to the sample to mask certain interferences.

3. Interferences

3.1 Iron, nickel, and cobalt at 100 μg/L and magnesium at 30 mg/L, in the prepared sample solution, interfere by suppressing the absorption of the chromium. These interferences are eliminated in solutions containing about 18,000 mg/L of ammonium chloride (Barnes, 1966, and Giammarise, 1966). Samples adjusted to this concentration of ammonium chloride show no interferences from 7×10^5 μg/L of iron and 10,000 μg/L each of nickel and cobalt, or from 1,000 mg/L of magnesium.

3.2 Individual concentrations of sodium (8,000 mg/L), calcium (4,000 mg/L), nitrate (100 mg/L), sulfate (8,000 mg/L), and chloride (10,000 mg/L) 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	357.9 nm.
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

4.3 The 102-mm, flathead, single-slot burner allows a working range of 10 to 400 μg/L. Different burners may be used according to manufacturers' instructions.

5. Reagents

5.1 *Ammonium chloride solution*, 200 g/L: Dissolve 200 g NH_4Cl in demineralized water and dilute to 1 L.

5.2 *Chromium standard solution I*, 1.00 mL= 100 μg Cr: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium standard solution II*, 1.00 mL= 1.00 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium standard working solutions*: Prepare a series of at least six standard working solutions containing from 10 to 400 μg/L of chromium by diluting chromium standard solution II. To each standard working solution, add 1.0 mL of NH_4Cl solution for each 10 mL of standard. Similarly, prepare a demineralized water blank.

6. Procedure

6.1 Add 1.0 mL NH_4Cl solution to 10.0 mL sample solution and mix thoroughly.

6.2 Aspirate the blank 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 chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method and multiply by the proper dilution factors.

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

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

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

8. Report

8.1 Report chromium, dissolved (01030), total-recoverable (01034), and suspended-recoverable (01031), concentrations as follows: less than 1,000 μg/L, nearest 10 μg/L: 1,000 μg/L and above, two significant figures.

8.2 Report chromium, recoverable-from-bottom-material (01029), concentrations as follows: less than 10 μg/g, nearest microgram per gram; 10 to 100 μg/g, nearest 10 μg/g; 100 μg/g and above, two significant figures.

9. Precision

9.1 The standard deviation for dissolved chromium within the range of 6.7 to 55 μg/L for 23 samples was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 7.2 μg/L ranged from 6.7 to 7.9 μg/L.

9.2 Precision for dissolved chromium for five of the 23 samples expressed in terms of the percent relative standard deviation is as follows:

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
6	6.7	77
23	10.9	54
23	18.7	46
13	30.2	19
6	55.0	19

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

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

Number of laboratories	Mean (μg/L)	Relative standard deviation (percent)
8	31.6	22
11	27.3	38

References

Barnes, L., Jr., 1966, Determination of chromium in low alloy steels by atomic absorption spectrometry: Analytical Chemistry, v. 38, p. 1083–1085.

Giammarise, A., 1966, The use of ammonium chloride in analyses of chromium samples containing iron: Atomic Absorption Newsletter, v. 5, p. 113–115.

Chromium, atomic absorption spectrometric, graphite furnace

Parameter and Code:
Chromium, dissolved, I-1235-85 (μg/L as Cr): 01030

1. Application

1.1 This method may be used to determine chromium in low ionic-strength water and precipitation. With deuterium background correction and a 20-μL sample, the method is applicable in the range from 0.2 to 20 μg/L. With Zeeman background correction and a 20-μL sample, the method is applicable in the range from 0.5 to 25 μg/L. Sample solutions that contain chromium concentrations exceeding the upper limits must be diluted or preferably be analyzed by the atomic absorption spectrometric direct or chelation-extraction method.

1.2 The analytical range and detection limits can be increased or possibly decreased by varying the volume of sample injected or the instrumental settings. Purification of reagents and use of ASTM Type 1 water (Method D-1193, American Society for Testing and Materials, 1984) may result in lower detection limits.

2. Summary of method

Chromium is determined by atomic absorption spectrometry in conjunction with a graphite furnace containing a graphite platform (Hinderberger and others, 1981). A sample is placed on the graphite platform and a matrix modifier is added. The sample is then evaporated to dryness, charred, and atomized using high-temperature ramping. The absorption signal generated during atomization is recorded and compared with standards.

3. Interferences

3.1 Interferences in low ionic-strength samples, such as precipitation, normally are quite low. In addition, the use of the graphite platform reduces the effects of many interferences. Calcium (25 mg/L), magnesium (8 mg/L), sodium (20 mg/L), sulfate (34 mg/L), and chloride (25 mg/L) do not interfere. Greater concentrations of these constituents were not investigated.

3.2 Precipitation samples usually contain very low concentrations of chromium. Special precautionary measures must be employed during both sample collection and laboratory determination to prevent contribution from contamination.

4. Apparatus

4.1 *Atomic absorption spectrometer*, for use at 357.9 nm and equipped with background correction, digital integrator to quantitate peak areas, graphite furnace with temperature programmer, and automatic sample injector. The programmer must have high-temperature ramping and stopped-flow capabilities.

4.1.1 Refer to the manufacturer's manual to optimize instrumental performance. The analytical ranges reported in paragraph 1.1 are for a 20-μL sample with 5 μL of matrix modifier (NOTE 1).

NOTE 1. A 20-μL sample generally requires 30 s to dry. Samples that have a complex matrix may require a longer drying and charring time.

4.1.2 *Graphite furnace*, capable of reaching temperatures sufficient to atomize the element of interest. Warning: dial settings frequently are inaccurate and newly conditioned furnaces require temperature calibration.

4.1.3 *Graphite tubes and platforms.* Pyrolytically coated graphite tubes and solid pyrolytic graphite platforms are recommended.

4.2 *Labware.* Many trace metals at very low concentrations have been found to sorb very rapidly to glassware. To preclude this, fluorinated ethylene propylene (FEP) or Teflon

labware may be used. Alternately, glassware, particularly flasks and pipets, may be treated with silicone anti-wetting agent such as Surfacil (Pierce Chemical Co., Rockford, IL, 61105) according to the manufacturer's instructions. Autosampler cups must be checked for contamination. Lancer (1831 Olive St., St. Louis, MO, 63103) polystyrene disposable cups have been found to be satisfactory after acid rinsing. Alternately, reuseable Teflon or FEP cups may be used.

4.3 *Argon*, standard, welder's grade, commercially available. Nitrogen may also be used if recommended by the instrument manufacturer.

5. Reagents

5.1 *Chromium standard solution I*, 1.00 mL=1,000 μg Cr: Dissolve 2.8290 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in Type 1 water. Add 10 mL high-purity, concentrated HNO_3 (sp gr 1.41), Ultrex or equivalent, and dilute to 1,000 mL with Type 1 water.

5.2 *Chromium standard solution II*, 1.00 mL=10.0 μg Cr: Dilute 10.0 mL chromium standard solution I to 1,000 mL (NOTE 2).

NOTE 2. Use acidified Type 1 water (paragraph 5.7) to make dilutions. All standards must be stored in sealed Teflon or FEP containers. Each container must be rinsed twice with a small volume of standard before being filled. Standards stored for 6 months in FEP containers yielded values equal to those of freshly prepared standards.

5.3 *Chromium standard solution III*, 1.00 mL=1.00 μg Cr: Dilute 100.0 mL chromium standard solution II to 1,000 mL. This standard is used to prepare working standards serially at time of analysis.

5.4 *Chromium standard solution IV*, 1.00 mL=0.01 μg Cr: Dilute 10.0 mL chromium standard solution III to 1,000 mL. This standard also is used to prepare working standards serially at time of analysis.

5.5 *Matrix modifier solution*, 4.0 g $Mg(NO_3)_2$/L, Suprapur MCB reagent or equivalent: Add 6.9 g $Mg(NO_3)_2 \cdot 6H_2O$ to 950 mL Type 1 water, mix, and dilute to 1,000 mL. DO NOT ADD ACID TO THE PURIFIED MATRIX MODIFIER SOLUTION.

5.6 *Nitric acid, concentrated*, high-purity, (sp gr 1.41): J. T. Baker "Ultrex" brand HNO_3 has been found to be adequately pure; however, each lot must be checked for contamination. Analyze acidified Type 1 water for chromium. Add an additional 1.5 mL of concentrated HNO_3/liter of water, and repeat analysis. Integrated signal should not increase by more than 0.001 absorbance-seconds.

5.7 *Water, acidified*, Type 1: Add 1.5 mL high-purity concentrated HNO_3 (sp gr 1.41) to each liter of water.

5.8 *Water, Type 1*

6. Procedure

6.1 Systematically clean and rinse work areas with deionized water on a regular schedule. Use a laminar flow hood or a "clean room" environment during sample transfers. Ideally, the autosampler and the graphite furnace should be in a clean environment.

6.2 Soak autosampler cups at least overnight in a 1 + 1 solution of Type 1 water and high-purity nitric acid.

6.3 Rinse the sample cups twice with sample before filling. Place cups in sample tray and cover. Adjust sampler so that only the injection tip contacts the sample.

6.4 In sequence, inject 20-μL aliquots of blank and working standards plus 5 μL of modifier each and analyze. Analyze the blank and working standards twice. Construct the analytical curve from the integrated peak areas (absorbance-seconds). Generally, the curve should be linear to a peak-absorbance (peak-height) value of 0.40 absorbance units.

6.5 Similarly, inject and analyze the samples twice. Every tenth sample cup should contain either a standard or a reference material.

6.6 Restandardize as required. Minor changes of values for known samples usually indicate deterioration of the furnace tube, contact rings, and/or platform. A major variation usually indicates either autosampler malfunction or residue buildup from a complex matrix in a previous sample.

7. Calculations

Determine the micrograms per liter of chromium in each sample from the digital display or printer output. Dilute those samples containing concentrations of chromium that exceed the

working range of the method; repeat the analysis, and multiply by the proper dilution factors.

8. Report

Report chromium, dissolved (01030), concentrations as follows: less than 10.0 µg/L, nearest 0.1 µg/L; 10 µg/L and above, two significant figures for both deuterium background correction and Zeeman background correction.

9. Precision

9.1 Analysis of one sample 15 times by a single operator using deuterium background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
13.87	0.95	6.8

9.2 Analysis of four samples six times each by a single operator using Zeeman background correction is as follows:

Mean (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)
7.30	0.17	2.3
11.63	.18	1.5
17.53	.16	.9
23.63	.20	.8

9.3 The precision and bias for the Zeeman background correction were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of chromium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.2	2.43	0.29	11.9	110
4.4	5.08	.37	7.3	115
8.0	7.6	.42	5.5	95
8.5	7.93	.64	8.1	93
16	15.38	.34	2.2	96
Tap water				
2.2	2.37	.51	21.5	108
4.4	4.53	.96	21.2	103
8.0	7.17	1.43	19.9	90
8.5	7.53	1.17	7.0	89
16	13.90	2.13	15.3	87

9.4 The precision and bias for the deuterium background method were tested on deionized water and tap water (specific conductance 280 µS/cm). A known amount of chromium was added to each sample, and single-operator precision and bias for six replicates are as follows:

Amount added (µg/L)	Amount found (µg/L)	Standard deviation (µg/L)	Relative standard deviation (percent)	Recovery (percent)
Deionized water				
2.2	2.22	0.41	18.5	101
4.4	4.79	.28	5.8	109
8.0	8.09	.46	5.7	101
8.5	7.92	.56	7.1	93
16	15.45	.91	5.9	97
Tap water				
2.2	2.49	.30	12.0	113
4.4	4.64	.56	12.1	105
8.0	7.48	.41	5.5	94
8.5	8.36	.56	6.7	98
16	14.58	1.08	7.4	91

9.5 The standard deviation from interlaboratory data, without regard to type of background correction and use of matrix modifiers, if any, for dissolved chromium within the range of 4.6 to 30.8 µg/L for 16 samples, was found to be independent of concentration. The 95-percent confidence interval for the average standard deviation of 5.0 µg/L ranged from 4.5 to 5.6 µg/L.

References

American Society for Testing and Materials, 1984, Annual book of ASTM standards, section 11, water: Philadelphia, v. 11.01, p. 39–41.

Cooksey, M., and Barnett, W. B., 1979, Matrix modification and the method of additions in flameless atomic absorption: Atomic Absorption Newsletter, v. 18, p. 101–5.

Fernandez, F. J., Beatty, M. M., and Barnett, W. B., 1981, Use of the L'vov platform for furnace atomic absorption applications: Atomic Spectroscopy, v. 2, p. 16–21.

Hinderberger, E. J., Kaiser, M. L., and Koirtyohann, S. R., 1981, Furnace atomic absorption analysis of biological samples using the L'vov platform and matrix modification: Atomic Spectroscopy, v. 2, p. 1–11.

Manning, D. C., and Slavin, W., 1983, The determination of trace elements in natural waters using the stabilized temperature platform furnace: Applied Spectroscopy, v. 37, p. 1–11.

Ottaway, J. M., 1982, A revolutionary development in graphite furnace atomic absorption: Atomic Spectroscopy, v. 3, p. 89–92.

Slavin, W., Carnrick, G. R., and Manning, D. C., 1982, Magnesium nitrate as a matrix modifier in the stabilized temperature platform furnace: Analytical Chemistry, v. 54, p. 621–4.

Chromium, total-in-sediment, atomic absorption spectrometric, direct

Parameter and Code:

Chromium, total I-5474-85 (mg/kg as Cr): none assigned

2. Summary of method

A sediment sample is dried, ground, and homogenized. The sample is digested with a combination of nitric, hydrofluoric, and perchloric acids in a Teflon beaker heated on a hotplate at 200 °C. Chromium 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.

Chromium, hexavalent, atomic absorption spectrometric, chelation-extraction

Parameter and Code:
Chromium, hexavalent, dissolved, I-1232-85 (μg/L as Cr): 01032

1. Application

1.1 This method may be used to analyze water and brines containing from 1 to 25 μg/L of chromium. Samples containing more than 25 μg/L need to be diluted prior to chelation-extraction.

1.2 If the iron concentration of the sample exceeds 5,000 μg/L, determine hexavalent chromium by the colorimetric diphenylcarbazide method (I-1230).

2. Summary of method

Hexavalent chromium is determined by atomic absorption spectrometry. The element is chelated with ammonium pyrrolidine dithiocarbamate (APDC) and extracted with methyl isobutyl ketone (MIBK). The extract is aspirated into the air-acetylene flame of the spectrometer (Midgett and Fishman, 1967).

3. Interferences

Concentrations of iron greater than 5,000 μg/L interfere by suppressing the chromium absorption.

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	357.9 nm
Source (hollow-cathode lamp)	Chromium
Oxidant	Air
Fuel	Acetylene
Type of flame	Reducing

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

5. Reagents

5.1 *Ammonium pyrrolidine dithiocarbamate (APDC) solution*, 1.0 g/100 mL: Dissolve 1.0 g APDC in demineralized water and dilute to 100 mL. Prepare fresh daily.

5.2 *Chromium standard solution I*, 1.00 mL=100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.3 *Chromium standard solution II*, 1.00 mL=10.0 μg Cr^{+6}: Dilute 100 mL chromium standard solution I to 1,000 mL with demineralized water.

5.4 *Chromium standard solution III*, 1.00 mL=0.10 μg Cr^{+6}: Dilute 10.0 mL chromium standard solution II to 1,000 mL with demineralized water.

5.5 *Methyl isobutyl ketone* (MIBK).

5.6 *Sodium hydroxide solution*, 2.5*M*: Dissolve 100 g NaOH in demineralized water and dilute to 1 L. Alternately a 2.5*M* NH_4OH solution may be used. Add 167 mL concentrated NH_4OH (sp gr 0.90) to 600 mL demineralized water. Mix, cool,and dilute to l L with demineralized water.

6. Procedure

6.1 Clean all glassware used in this determination with warm, dilute HNO_3 (1+9) and rinse with demineralized water immediatley before use.

6.2 Pipet a volume of sample containing less than 2.5 μg Cr^{+6} (100 mL max) into a 200-mL volumetric flask, and adjust the volume to approx 100 mL.

6.3 Acidify a liter of demineralized water with 1.5 mL concentrated HNO_3 (sp gr 1.41). Prepare a blank and at least six standards containing from 1 to 25 μg/L of Cr^{+6}, and adjust the volume of each to approx 100 mL with the acidified demineralized water.

6.4 With a pH meter, adjust the pH of each solution to 2.4 by dropwise addition of 2.5*M* NaOH or NH_4OH.

6.5 Add 5.0 mL APDC solution and mix.

6.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

6.7 Allow the layers to separate and add demineralized water until the ketone layer is completely in the neck of the flask. The Cr^{+6}-APDC complex is stable for at least 36 h.

6.8 Aspirate the ketone layer of the blank to set the automatic zero control. Use the automatic concentration control to set the concentrations of 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

Determine the micrograms per liter of hexavalent chromium in each sample from the digital display or printer while aspirating each sample. Dilute those samples containing chromium concentrations that exceed the working range of the method; repeat the chelation-extraction and multiply by the proper dilution factor.

8. Report

Report chromium, dissolved, hexavalent (01032), concentrations as follows: less than 10 μg/L, nearest microgram per liter; 10 μg/L and above, two significant figures.

9. Precision

It is estimated that the precision of this method for Cr^{+6} is equal to total chromium by the atomic absorption spectrometric chelation-extraction method.

Reference

Midgett, M. R., and Fishman, M. J., 1967, Determination of total chromium in fresh waters by atomic absorption: Atomic Absorption Newsletter, v. 6, p. 128-131.

Chromium, hexavalent, colorimetric, diphenylcarbazide

Parameter and Code:

Chromium, hexavalent, dissolved, I-1230-85 (μg/L as Cr^{+6}): 01032

1. Application

This method may be used to analyze most natural water containing from 50 to 4,000 μg/L hexavalent chromium. Samples containing higher concentrations must first be diluted.

2. Summary of method

2.1 This method determines only hexavalent chromium in solution.

2.2 In acid solution, diphenylcarbazide and hexavalent chromium form a soluble red- violet product that absorbs light at 540 nm. The pH of the reaction is not particularly critical; solutions differing in pH from 0.7 to 1.3 give identical colors. The color of the chromium-diphenylcarbazide product changes slightly with time, but for practical purposes it can be considered stable.

2.3 Additional information on the principle of the determination is given by Sandell (1950).

3. Interferences

For all practical purposes the reaction is specific for chromium; metallic interference almost never occurs. Iron, mercury, and molybdenum in concentrations as high as 100,000 μg/L show only a small effect. Vanadium should not be present in concentrations exceeding 4,000 μg/L. The effect of water color is small, and color as much as 50 color units (Hazen scale) is tolerable. The chromium color develops almost instantly and is stable; whereas, vanadium color develops instantly and then fades rapidly. If the original vanadium concentration is less than 4,000 μg/L, no vanadium color persists after 10 min.

4. Apparatus

4.1 *Spectrometer* for use at 540 nm.

4.2 Refer to the manufacturer's manual for optimizing instrument.

5. Reagents

5.1 *Chromium standard solution*, 1.00 mL= 100 μg Cr^{+6}: Dissolve 0.2829 g primary standard $K_2Cr_2O_7$, dried for 1 h at 180°C, in demineralized water and dilute to 1,000 mL.

5.2 *Diphenylcarbazide reagent*: Dissolve 0.2 g diphenylcarbazide and 1.0 g phthalic anhydride in 200 mL ethanol. This reagent is stable for several weeks; a slight discoloration will not impair the usefulness of the reagent.

5.3 *Sulfuric acid*, 1.2*M*: **CAUTIOUSLY**, add 6.5 mL concentrated H_2SO_4 (sp gr 1.84) to demineralized water and dilute to 100 mL.

6. Procedure

6.1 Pipet a volume of sample containing less than 40 μg Cr^{+6} (10.0 mL max) into a 50-mL beaker, and adjust the volume to 10.0 mL with demineralized water.

6.2 Prepare a blank of demineralized water and sufficient standards, and adjust the volume of each to 10.0 mL with demineralized water.

6.3 Add 1.0 mL 1.2*M* H_2SO_4 and mix.

6.4 Add 0.5 mL diphenylcarbazide reagent and mix.

6.5 Allow to stand 10 min.

6.6 Determine the absorbance of the sample and standards against the blank, and when necessary make a correction for water color.

7. Calculations

7.1 Determine micrograms hexavalent chromium in the sample from a plot of absorbances of standards.

7.2 Determine the hexavalent chromium concentration in micrograms per liter as follows:

$$Cr^{+6}\ (\mu g/L) = \frac{1{,}000 \times \mu g\ Cr^{+6}\ \text{in sample}}{\text{mL sample}}$$

8. Report

Report chromium, dissolved hexavalent (01032), concentrations as follows: 50 to 100 μg/L, nearest 10 μg/L; 100 μg/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 (μg/L)	Relative standard deviation (percent)
5	810	5

Reference

Sandell, E. B., 1950, Colorimetric determination of traces of metals (2d ed.): New York, Interscience Publishers, p. 260.