

METHOD 9251

CHLORIDE (COLORIMETRIC, AUTOMATED FERRICYANIDE AAI)

1.0 SCOPE AND APPLICATION

1.1 This automated method is applicable to ground water, drinking, surface, and saline waters, and domestic and industrial wastes. The applicable range is 1-200 mg Cl⁻ per liter of sample.

2.0 SUMMARY OF METHOD

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

3.0 INTERFERENCES

3.1 No significant interferences.

4.0 APPARATUS AND MATERIALS

4.1 Automated continuous-flow analytical instrument:

4.1.1 Sampler I.

4.1.2 Analytical cartridge.

4.1.3 Proportioning pump.

4.1.4 Colorimeter: Equipped with 15-mm tubular flowcell and 480-nm filters.

4.1.5 Recorder.

4.1.6 Digital printer (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Mercuric thiocyanate solution: Dissolve 4.17 g of Hg(SCN)₂ in 500 mL methanol. Dilute to 1 liter with methanol, mix, and filter through filter paper.

5.3 Ferric nitrate solution, 20.2%: Dissolve 202 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 500 mL of Type II water. Add 31.5 mL concentrated nitric acid, mix, and dilute to 1 liter with Type II water.

5.4 Color reagent: Add 150 mL of mercuric thiocyanate solution (Paragraph 5.2) to 150 mL of ferric nitrate solution (Paragraph 5.3), mix, and dilute to 1 liter with Type II water. A combined color reagent is commercially available.

5.5 Sodium chloride stock solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in Type II water. Dilute to 1 liter in a volumetric flask (1 mL = 0.5 mg Cl^-).

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

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

Choose three of the nine standard concentrations in such a way that the chosen standards will bracket the expected concentration range of the sample.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 No special requirements for preservation.

7.0 PROCEDURE

7.1 When particulate matter is present, the sample must be filtered prior to the determination. The sample may be centrifuged in place of filtration. Set up the manifold, as shown in Figure 1.

7.2 Allow both colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding Type II water through the sample line.

7.3 Place working standards in sampler in order of decreasing concentrations. Complete filling of sampler tray with unknown samples.

7.4 When a stable baseline has been obtained, start the sampler.

7.5 Calculation: Prepare standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of samples by comparing sample peak heights with standard curve. Note that this is not a linear curve, but a second order curve. (See Paragraph 8.2.)

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. O'Brien, J.E., "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).
2. Technicon AutoAnalyzer II, Industrial Method No. 99-70W, Technicon Industrial Systems, Tarrytown, New York, 10591 (Sept. 1973).

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