

## METHOD 9250

### 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 to 250 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 Continuous filter.

4.1.3 Manifold.

4.1.4 Proportioning pump.

4.1.5 Colorimeter: equipped with 15-mm tubular flowcell and 480-nm filters.

4.1.6 Recorder.

#### 5.0 REAGENTS

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

5.2 Ferric ammonium sulfate: Dissolve 60 g of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  in approximately 500 mL Type II water. Add 355 mL of concentrated  $\text{HNO}_3$  and dilute to 1 liter with Type II water. Filter.

5.3 Saturated mercuric thiocyanate: Dissolve 5 g of  $\text{Hg}(\text{SCN})_2$  in 1 liter of Type II water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

5.4 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).

5.4.1 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
50.0	250.0

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 No advance sample preparation is required. Set up manifold, as shown in Figure 1. For water samples known to be consistently low in chloride content, it is advisable to use only one Type II water intake line.

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. Adjust dark current and operative opening on colorimeter to obtain stable baseline.

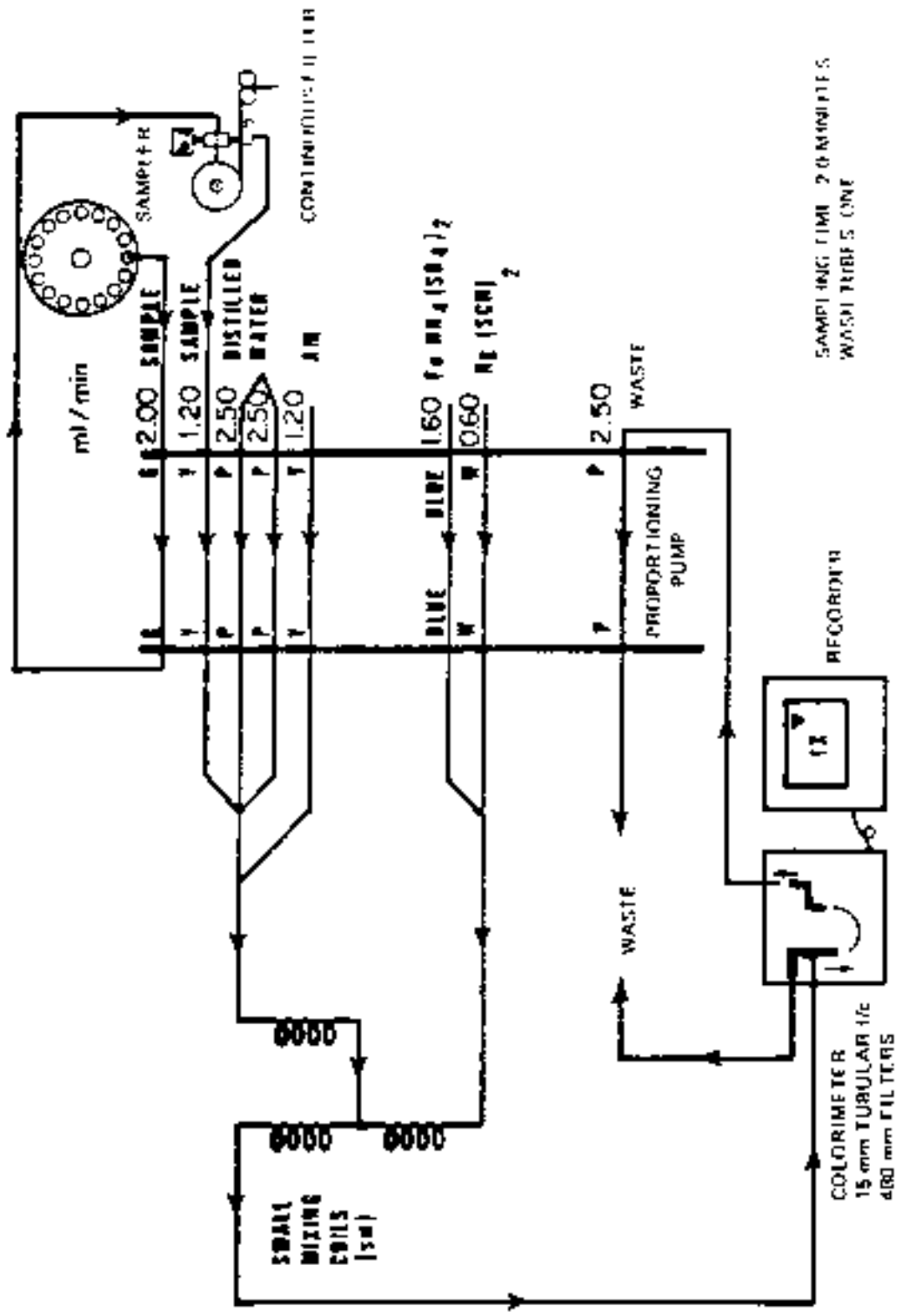


FIGURE 1. CHLORIDE MANIFOLD AA-1

7.3 Place Type II water wash tubes in alternate openings in sampler and set sample timing at 2.0 min.

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

7.5 Switch sample line from Type II water to sampler and begin analysis.

7.6 Calculation:

7.6.1 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.

## 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 available in Method 325.1 of Methods for Chemical Analysis of Water and Wastes.

## 10.0 REFERENCES

1. O'Brien, J.E., "Automatic Analysis of Chlorides in Sewage," Waste Engr., 33, 670-672 (Dec. 1962).
2. Standard Methods for the Examination of Water and Wastewater, 14th ed., p. 613, Method 602 (1975).

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