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.

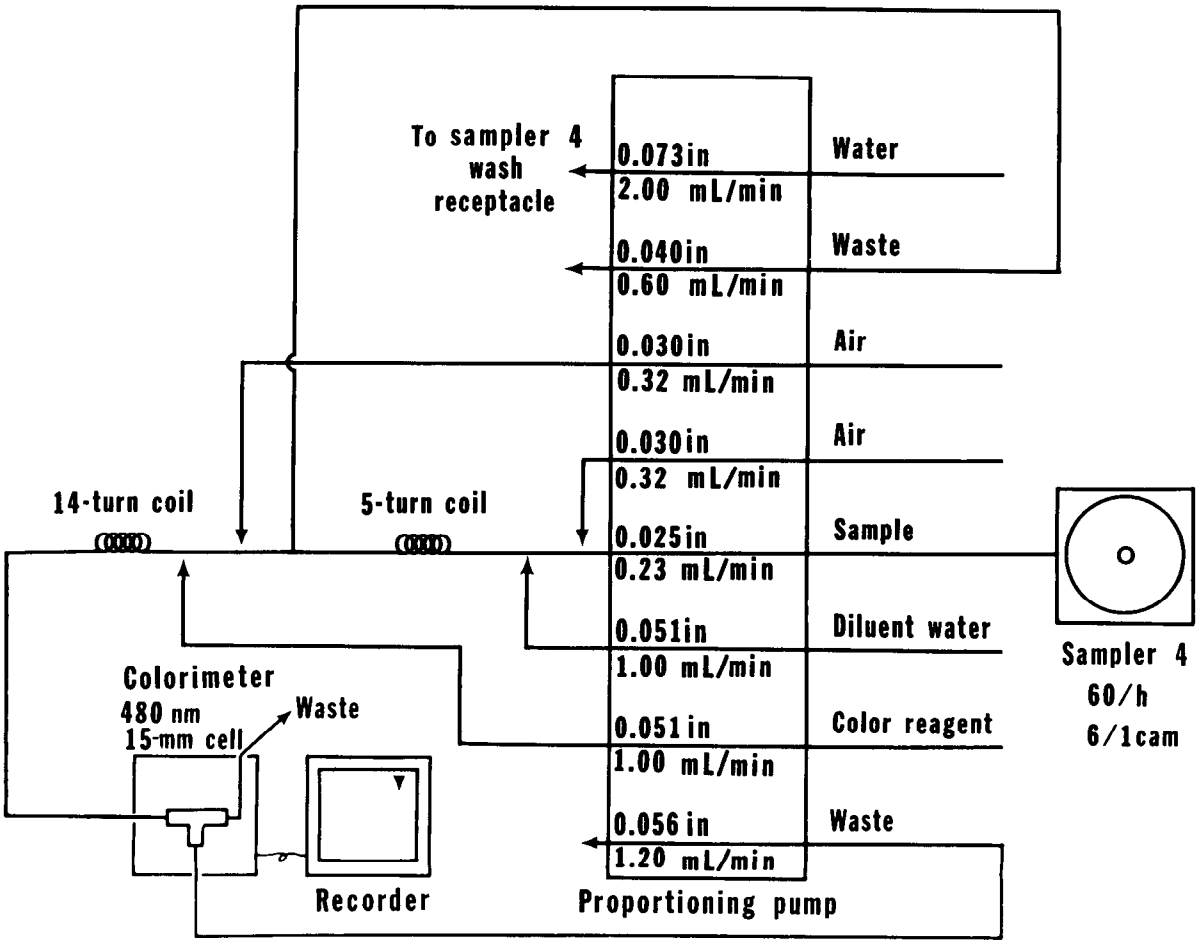

Figure 20.—Chloride, ferric thiocyanate manifold

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.