METHOD #: 325.1	Approved for NPDES (Issued 1971)	
TITLE:	Chloride (Colorimetric, Automated Ferricyanide AAI)	
ANALYTE:	CAS # Cl- Chloride 16887006	
INSTRUMENTATION:	Autoanalyzer	
STORET No.	00940	

- 1.0 Scope and Application
 - 1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 1 to 250 mg Cl/L. Approximately 15 samples per hour can be analyzed.
- 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 concentration proportional to the original chloride concentration.
- 3.0 Sample Handling and Preservation
 - 3.1 No special requirements.
- 4.0 Interferences
 - 4.1 No significant interferences.

5.0 Apparatus

- 5.1 Technicon AutoAnalyzer consisting of:
 - 5.1.1 Sampler I.
 - 5.1.2 Continuous filter.
 - 5.1.3 Manifold.
 - 5.1.4 Proportioning pump.
 - 5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 480 nmfilters.
 - 5.1.6 Recorder.
- 6.0 Reagents
 - 6.1 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 distilled water. Add 355 mL of conc. HNO_3 and dilute to 1 liter with distilled water. Filter.
 - 6.2 Saturated Mercuric Thiocyanate: Dissolve 5 g of Hg(SCN)₂ in 1 liter of distilled

water. Decant and filter a portion of the saturated supernatant liquid to use as the reagent and refill the bottle with distilled water.

- 6.3 Stock Solution (0.0141 N NaCl): Dissolve 0.8241 g of pre-dried (140°C) NaCl in distilled water. Dilute to 1 liter in a volumetric flask. 1 mL = 0.5 mg Cl.
 - 6.3.1 Prepare a series of standards by diluting suitable volumes of stock solution to 100.0 mL with distilled water. The following dilutions are suggested:

mL of Stock Solution	Conc., mg/L	
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	

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 distilled water intake line.
- 7.2 Allow both colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line. Adjust dark current and operative opening on colorimeter to obtain stable baseline.
- 7.3 Place distilled water wash tubes in alternate openings in sampler and set sample timing at 2.0 minutes.
- 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 distilled water to sampler and begin analysis.

8.0 Calculation

- 8.1 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.
- 9.0 Precision and Accuracy
 - 9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 1, 100, and 250 mg Cl/L, the standard deviation was ±0.3.
 - 9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 10 and 100 mg Cl/L, recoveries were 97% and 104%,respectively.

Bibliography

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

