METHOD #: 335.1 Approved for NPDES (Issued 1974)

TITLE: Cyanides, Amenable To Chlorination (Titrimetric;

Spectrophotometric)

ANALYTE: CN Cyanide

INSTRUMENTATION: Spectrophotometer

STORET No. 00722

1.0 Scope and Application

1.1 This method is applicable to the determination of cyanides amenable to chlorination in drinking, surface and saline waters, domestic and industrial wastes.

1.2 The titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/L after removal of the cyanides amenable to chlorination. Below this level the colorimetric determination is used.

2.0 Summary of Method

2.1 A portion of the sample is chlorinated at a pH > 11 to decompose the cyanide. Cyanide levels in the chlorinated sample are then determined by the method for Cyanide, Total, in this manual. Cyanides amenable to chlorination are then calculated by difference.

3.0 Reagents

- 3.1 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite (Ca(OCl)₂) in 100 mL of distilled water.
- 3.2 Sodium Hydroxide solution: Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 liter.
- 3.3 Ascorbic acid: crystals.
- 3.4 Potassium Iodide-starch test paper.

4.0 Procedure

- 4.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 mL aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (3.1) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (3.2).

 Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.
- 4.2 Test for residual chlorine with KI-starch paper (3.4) and maintain this excess

- for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.
- 4.3 After one hour, add 0.5 g portions of ascorbic acid (3.3) until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to insure the presence of excess reducing agent.
- 4.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots as in the method Cyanide, Total, in this manual.

5.0 Calculation

5.1 Calculate the cyanide amendable to chlorination as follows:

$$CN$$
, $mg/L = A - B$

where:

A = mg/L total cyanide in unchlorinated aliquot

B = mg/L total in chlorinated aliquot

Bibliography

- 1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2036-75, Method B, p 505 (1976).
- 2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 376 and 370, Method 413F and D (1975).