

METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewaters, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure provided in Method 9010.

3.2 Refer to Method 9010 for a discussion of potential cyanide interferences.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Refrigerator.

- 4.5 5 mL microburette.
- 4.6 Class A volumetric flasks - 1000, 250, and 100 mL.
- 4.7 Erlenmeyer flask - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for spectrophotometric determination

5.3.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.3.2 Sodium phosphate monobasic (1M), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. Dissolve 138 g of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 1 liter of water. Refrigerate this solution.

5.3.3 Chloramine-T solution (0.44%), $\text{C}_7\text{H}_7\text{ClNNaO}_2\text{S}$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.3.4 Pyridine-Barbituric acid reagent, $\text{C}_5\text{H}_5\text{N} \cdot \text{C}_4\text{H}_4\text{N}_2\text{O}_3$. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.5 Stock potassium cyanide solution (1 mL = 1000 $\mu\text{g CN}^-$), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, AgNO_3 . Dilute to appropriate concentration to achieve 1 mL = 1000 $\mu\text{g of CN}^-$.

NOTE: Detailed procedure for AgNO_3 standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Methods 4500-CN D.

5.3.6 Intermediate standard potassium cyanide solution, (1 mL = 100 $\mu\text{g CN}^-$), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 $\mu\text{g CN}^-$) to 1000 mL with water.

5.3.7 Working standard potassium cyanide solution, (1 mL = 10 $\mu\text{g CN}^-$), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

5.4 Reagents for titration procedure

5.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino-benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.4.2 Standard silver nitrate solution (0.0192N), $AgNO_3$. Prepare by crushing approximately 5 g $AgNO_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Method 4500-CN D.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9010 for guidance on sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at 4 °C.

7.0 PROCEDURE

7.1 If the manual spectrophotometric determination will be performed, proceed to Section

7.2. If the titration procedure will be performed, proceed to Section 7.6.

7.2 Manual spectrophotometric determination

7.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.3 Standard curve for samples without sulfide

7.3.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

<u>mL of Working Standard Solution</u> <u>(1 mL = 10 µg CN⁻)</u>	<u>Concentration</u> <u>(µg CN⁻/L)</u>
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.3.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Sections 7.2.2 and 7.2.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.3.3 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.4 Standard curve for samples with sulfide

7.4.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.4.2 Prepare a series of standards similar in concentration to those mentioned in Section 7.3.1 and analyze as in Section 7.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.5 Calculation - If the spectrophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$\text{CN}^- (\mu\text{g/L}) = \frac{A \times B \times C}{D \times E}$$

where:

- A = µg/L CN⁻ read from standard curve.
- B = mL of sample after preparation of colorimetric analysis (100 mL recommended).

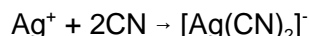
- C = mL of sample after distillation (250 mL recommended).
 D = mL of original sample for distillation (500 mL recommended).
 E = mL used for colorimetric analysis (50 mL recommended).

7.6 Titration Procedure

7.6.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.6.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL buret may be conveniently used to obtain a precise titration.

NOTE: The titration is based on the following reaction:



When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.6.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN^- in $\mu\text{g/L}$ in the original sample as follows:

$$\text{CN}^- (\mu\text{g/L}) = \frac{(A - B)}{C} \times D \times \frac{E}{F} \times \frac{2 \text{ mole CN}^-}{1 \text{ eq. AgNO}_3} \times \frac{26.02 \text{ g CN}^-}{1 \text{ mole CN}^-} \times \frac{1 \times 10^6 \mu\text{g}}{1 \text{ g}}$$

where:

- A = mL of AgNO_3 for titration of sample.
 B = mL of AgNO_3 for titration of blank.
 C = mL of sample titrated (250 recommended).
 D = actual normality of AgNO_3 (0.0192N recommended).
 E = mL of sample after distillation (250 recommended).
 F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

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

8.2 Refer to the quality control section of Method 9010A for the method requirements for blanks, matrix duplicates, and matrix spikes. Each QC sample must be processed through the reflux-distillation steps contained in Method 9010 prior to analysis by this method.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Analyze one replicate sample for every 20 samples. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Analyze one matrix spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^- , the standard deviations for precision were ± 0.005 to ± 0.094 , respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^- , recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

10.1 Refer to Method 9010 for references on total and amenable cyanide.

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