Cyanide, colorimetric, pyridine-pyrazolone

Parameters and Codes:
Cyanide, dissolved, I-1300-85 mg/L as CN): 00723
Cyanide, total, I-3300-85 (mg/L as CN): 00720
Cyanide, total-in-bottom-material, dry wt, I-5300-85 (mg/kg as CN): 00721

1. Application

1.1 The method may be used to determine cyanide in water and water-suspended sediment containing at least 0.01 mg/L of cyanide.

1.2 This method may be used to determine cyanide in bottom material containing at least 0.5 mg/kg.

1.3 Total cyanide in water-suspended sediment may be determined if each sample is shaken vigorously and a suitable aliquot of well mixed sample withdrawn.

2. Summary of method

This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye. The method detects only simple cyanides; therefore, any complex cyanides present must be broken down. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure. The distillation also removes certain interferences from water samples.

3. Interferences

3.1 Common interferences include sulfide, heavy-metal ions, fatty acids, steam-distillable organic compounds, cyanate, thiocyanate, glycine, urea, oxidizing agents, and substances that may contribute color or turbidity to the sample.

3.2 These interferences may be removed or their effect minimized as follows:

3.2.1 Sulfide can be removed as lead sulfide by adding a slight excess of lead carbonate to 400 mL of the alkaline (pH 11.0 or above) sample. Filter the sample immediately, wash the precipitate with demineralized water, and add the washings to the filtrate.

3.2.2 Fatty acids can be removed by acidifying 400 mL of sample with acetic acid to a pH of between 6 and 7, and by extracting with 80 mL of either isooctane or hexane. A single extraction is usually sufficient.

3.2.3 Oxidizing agents can be removed by adding sodium sulfite solution to 400 mL of sample until a negative test with starch-iodide paper is obtained.

3.2.4 Most remaining interferences are removed by the distillation.

3.3 This method includes no provisions for removing these interferences or for minimizing their effects in water-suspended sediment and bottom material. The analyst must be aware that, when such interfering substances are present, the analytical result obtained may be in error, although distillation of the cyanide certainly separates it from some of the interfering substances.

4. Apparatus

4.1 *Distillation train* (fig. 1). An efficient gas washer is essential to the proper operation of the distillation assembly. The Fisher-Milligan unit has been found satisfactory.

4.2 *Heating element* for Claisen flask.

4.3 *Spectrometer* for use at 620 nm.

4.4 Refer to the manufacturer's manual to optimize instrument.

5. Reagents

5.1 *Acetic acid*, 3*M*: Mix 172 mL glacial $HC_2H_3O_2$ (sp gr 1.06) with demineralized water and dilute to 1 L.
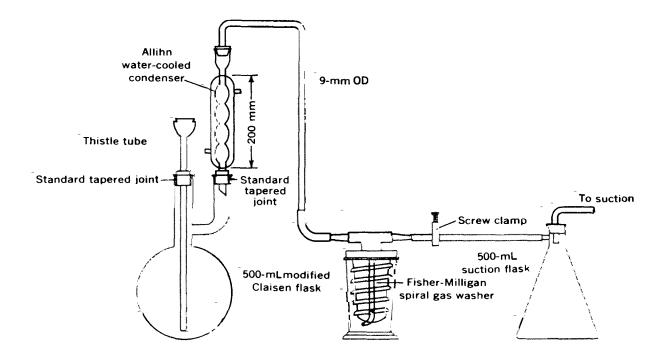
Figure 1.-Cyanide, distillation train

5.2 *Chloramine-T solution,* 1 g/100 mL: Dissolve 0.25 g chloramine-T in 25 mL demineralized water. This solution is unstable and must be prepared immediately before use. When a blank and standards are used, the chloramine-T solution may be used throughout a period of several hours, but each succeeding use results in lower absorbance readings for the same concentration of cyanide.

5.3 *Cyanide standard solution I,* 1.00 mL = 1.00 mg CN: Dissolve 2.50 g KCN (NOTE 1) in 1 L demineralized water. Standardize with silver nitrate standard solution, 1.00 mL = 1.00 mg CN, as follows: Adjust the pH of 5.0 mL cyanide standard solution I to 11.0 or above, and dilute to 250 mL with demineralized water. Add 0.5-1.0 mL 5-(p-dimethyl-aminobenzylidene) rhodamine indicator solution and titrate with standard silver nitrate solution to the first color change from canary yellow to salmon. Subtract the blank obtained by titrating an identical volume of water, alkali, and indicator. The cyanide solution is unstable and must be either restandardized weekly or prepared fresh when needed.

NOTE 1. CAUTION-POISON: May be fatal if swallowed or inhaled. Contact with acid liberates poisonous gas. Contact with KCN may burn eyes and irritate skin.

5.4 *Cyanide standard solution II,* 1.00 mL = 0.010 mg CN: Add 10.0 mL cyanide standard solution I to demineralized water and dilute to 1,000 mL. This solution must be prepared fresh before use.

5.5 *Cyanide standard solution III,* 1.00 mL = 0.001 mg CN: Add 10.0 mL cyanide standard solution II to demineralized water and dilute to 100 mL. This solution mu st be prepared fresh before use.

5.6 *Magnesium chloride solution,* 24 g/100 mL: Dissolve 51 g $MgCl_2 \cdot 6H_2O$ in 100 ML demineralized water.

5.7 *5-(p-Dimethylaminobenzylidene)rhodamine indicator solution,* 0.02 g/100 mL: Dissolve 0.02 g 5-1p-dimethylaminobenzy lidene)rhodamine in 100 mL acetone. Eastman Kodak No. 2748 has been found satisfactory.

5.8 *Pyrazolone solution I:* Add 0.8 g 1-phenyl-3-methyl-5-pyrazolone to 150 mL de-mineralized water at 75°C. Cool to room temperature, with stirring; filter. Eastman Kodak No. 1397 has been found satisfactory.

5.9 *Pyrezolone solution II:* Dissolve 0.025 g bis-pyrazolone in 25 mL pyridine and filter. Eastman Kodak No. 6969 has been found satisfactory. Several minutes of mixing are usually required to effect solution.

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5.10 *Pyridine pyrazolone reagent:* Mix 125 mL pyrazolone solution I with 25 mL pyrazolone solution II. After standing, the mixed reagent develops a pink color which does not affect color development. Prepare this reagent fresh daily or before each use.

5.11 *Pyridine.*

5.12 *Silver nitrate standard solution,* 1.00 mL 1.00 mg CN: Crush approx 5 g of $AgNO_3$ crystals and dry to constant mass at 40°C. Dissolve 3.2647 g $AgNO_3$ in demineralized water and dilute to 1 L. This solution is needed only to standardize the cyanide standard solution I.

5.13 *Sodium hydroxide,* 1*M*: Dissolve 4 g NaOH in 100 mL demineralized water.

5.14 *Sulfuric acid,* concentrated (sp gr 1.84).

6. Procedure

6.1 *Distillation:* Follow instructions in paragraph 6.1.1 for water or water-suspended sediment and paragraph 6.1.2 for bottom material, after assembling the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator.

6.1.1 Add 400 mL water or water-suspended sediment (or smaller aliquot diluted to 400 mL) to the boiling flask.

6.1.2 Add a weighed portion (5-10g) of bottom-material and 250-500 mL demineralized water to the boiling flask.

6.2 Add exactly 50 mL 1*M* NaOH and 100 mL demineralized water to the gas washer. Connect train and adjust suction so that 1 or 2 bubbles per second enter the boiling flask through the air inlet. Do not increase airflow beyond 2 bubbles per second.

6.3 Add 10 mL $MgCl_2$ solution through the thistle tube, and allow the airflow to mix for 3 min. Rinse air tube with demineralized water, then slowly add 20 mL concentrated H_2SO_4. Rinse the tube again.

6.4 Heat at a rate that produces rapid boiling, but not enough to flood the condenser inlet or permit the vapors to rise more than halfway into the condenser. Reflux for 1 h. Turn off heat, but permit airflow to continue for 15 min.

6.5 Transfer gas washer contents to a 200-mL volumetric flask. Wash the tube, from the condenser to the gas washer, and the gas washer with small amounts of demineralized water and add to contents of flask. Dilute contents of volumetric flask to 200 mL.

6.6 Refill the gas washer with NaOH and demineralized water, as in 6.2, and repeat reflux procedure. If only readily hydrolyzed cyanides are present, the absorber liquid from the first reflux period will contain all the available cyanide. If stable complex cyanides are present, a measurable yield will appear in the absorber liquid during the second and succeeding reflux periods, depending on the degree of stability of the compounds.

6.7 *Colorimetric procedure:* The standards and many of the reagents used in this procedure are unstable and must be prepared immediately before use if maximum color development is to be obtained. The color development is also dependent on the presence of approximately equal total-salt concentrations in both samples and standards. If the final distillate volume is 200 mL, it will be about 0.25*M* in NaOH. For this reason 0.25*M* NaOH must be used for dilutions and for the standards and blank. Any substantial deviation in the quantity of 3*M* $HC_2H_3O_2$ required to neutralize blank and standards will require additional manipulation to bring these volumes into approximate agreement. The variation should be less than 0.3 mL.

6.8 Prepare a blank by pipetting 15 mL of 0.25*M* NaOH into a 23-mm absorption cell fitted with a rubber stopper. Prepare standards containing 0.0005 mg and 0.001 mg CN, each diluted to 15 mL with 0.25*M* NaOH in similar containers.

6.9 Take 15-mL aliquots (or smaller volumes diluted to 15 mL with 0.25*M* NaOH) of the distillates from the purification procedure and place in 23-mm stoppered absorption cells.

6.10 Neutralize each sample, blank, and standard with 3*M* $HC_2H_3O_2$ using phenolphthalein indicator solution.

6.11 To each sample, blank, and standard add 4 drops chloramine-T solution, stopper, and shake. Allow 2 min for the reaction to proceed.

6.12 Add 5.0 mL pyridine-pyrazolone reagent and mix well. Allow 20 min for color development.

6.13 Read absorbances at 620 nm. The color is stable for 30 min. The absorbance decreases

slowly over a period of 3 h and can probably be read during this period with some decrease in accuracy.

7. Calculations

7.1 Determine the concentration of dissolved or total cyanide in milligrams per liter as follows:

$$CN(mg/L) = \frac{1000}{mL\ original\ sample} \times \frac{mL\ distillate}{mL\ aliquot}$$

$$\times \frac{A_{sample}}{A_{std.}} \times mg\ standard$$

where

A_{sample} = absorbance of sample,
and
$A_{std.}$ = absorbance of standard.

7.2 Determine the concentration of cyanide in bottom-material samples in milligrams per kilogram as follows:

$$CN(mg/L) = \frac{1000}{wt\ of\ sample\ (g)} \times \frac{mL\ distillate}{mL\ aliquot}$$

$$\times \frac{A_{sample}}{A_{std.}} \times mg\ standard$$

where

A_{sample} = absorbance of sample,
and
$A_{std.}$ = absorbance of standard.

8. Report

8.1 Report cyanide, dissolved (00723) and total (00720), concentrations as follows: less than 1.0 mg/L, nearest 0.01 mg/L;1.0 mg/L and above, two significant figures.

8.2 Report cyanide, total-in-bottom-material (00721), concentrations as follows: less than 10 mg/kg, nearest 0.1 mg/kg; 10 mg/kg and above, two significant figures.

9. Precision

Precision data are not available for this method.