Cyanide, colorimetric, barbituric acid, automated-segmented flow

Parameters and Codes:
Cyanide, dissolved, I-2302-85 (mg/L as CN): 00723
Cyanide, total recoverable, I-4302-85 (mg/L as CN): 00720
Cyanide, recoverable-from-bottom-material, dry wt, I-6302-85 (mg/kg as CN): 00721

1. Application

1.1 This method may be used to analyze water and water-suspended sediment containing from 0.01 to 0.30 mg/L cyanide. Samples containing more than 0.30 mg/L need to be diluted.

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sediment can be determined if each sample is shaken vigorously and a suitable aliquot of well-mixed sample withdrawn.

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

2. Summary of method

This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent (Goulden and others, 1972). This method detects simple cyanides only; therefore, any complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure. The distillation step also removes certain interferences.

3. Interferences

3.1 Chloride interferes if its concentration exceeds 3,000 mg/L.

3.2 Oxidizing agents may interfere.

3.3 Glycine and urea at the 10-mg/L level do not interfere.

3.4 A concentration of 10 mg/L sulfide increases the apparent cyanide concentration by approx 0.02 mg/L. Concentrations of sulfide greater than 10 mg/L interfere considerably.

3.5 Thiocyanate is broken down to cyanide and sulfide by this procedure and, therefore, interferes on an equimolar basis.

3.6 Sulfate concentrations of 4,000 mg/L do not interfere. Higher concentrations were not tested.

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. This apparatus is for use only with bottom materials.

4.2 *Heating element* for Claisen flask.

4.3 *Technicon AutoAnalyzer II*, consisting of sampler, cartridge manifold with ultraviolet digestor, proportioning pump, heating bath with distillation head, voltage stabilizer, recorder, and printer.

4.4 With this equipment the following operating conditions have been found satisfactory for the range from 0.01 to 0.30 mg/L CN:

Absorption cell -------------- 15 mm
Wavelength ------------------ 570 nm
Cam ---------------------------20/h (6/1)
Heating-bath temperature ---155°C

5. Reagents

5.1 *Chloramine-T solution,* 4.0 g/L: Dissolve 2.0 g chloramine-T in demineralized water and dilute to 500 mL.

5.2 *Cyanide standard solution I*, 1.00 mL = 0.100 mg CN: Dissolve 0.2500 g KCN (NOTE 1) in O.1*M* NaOH and dilute to 1,000 mL with O.1*M* NaOH. Discard after 3 months.

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 akin.**

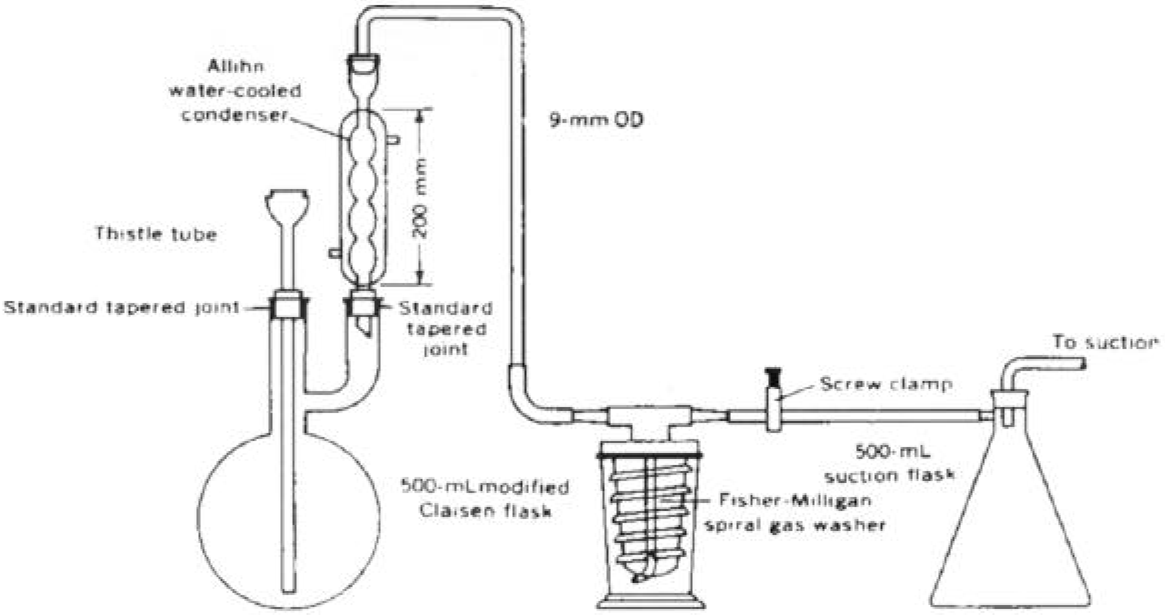

Figure 1. - Cyanide, distillation train

5.3 *Cyanide standard solution II,* 1.00 mL =0.002 mg CN: Add 20 mL cyanide standard solution I to 800 mL O.1*M* NaOH and dilute to 1,000 mL with O.1*M* NaOH. Prepare fresh daily.

5.4 *Cyanide working standards:* Prepare fresh daily, a blank and 100 mL each of a series of cyanide working standards by appropriate quantitative dilution of cyanide standard solution II as follows:

Cyanide Standard Solution II (ml)	Cyanide Concentration (mg/L)
1.0	0.020
2.0	0.040
5.0	0.100
10.0	0.200
15.0	0.300

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

5.6 *Phosphate buffer solution:* Dissolve 13.6 g KH_2PO_4 and 0.28 g Na_2HPO_4 in demineralized water and dilute to 1 L. Add 0.5 mL Brij -35 solution and mix.

5.7 *Phosphoric acid-hypophosphorous acid distillation reagent:* Carefully add 250 mL concentrated H_3PO_4 (sp gr 1.69) and 50 mL hypophosphorous acid to approx 700 mL demineralized water. Dilute to 1 L with demineralized water.

5.8 *Pyridine-barbituric acid solution:* Place 15 g barbituric acid in a 1-L beaker and add enough demineralized water (about 100 mL) to wash the sides of the beaker and wet the barbituric acid. Add 75 mL pyridine and mix. Add 15 mL concentrated HCl (sp gr 1.19) and mix. Dilute to about 900 mL with demineralized water and mix until all the barbituric acid has dissolved. Transfer the solution to a 1,000-mL volumetric flask and dilute to volume with demineralized water.

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

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

6. Procedure

6.1 For water or water-suspended sediment proceed to paragraph 6.2. For bottom material proceed as follows:

6.1.1 Assemble the distillation train, consisting of Claisen flask, thistle tube, condenser, gas washer, screw clamp, suction flask, and aspirator (fig. 21).

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

6.1.3 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.

6.1.4 Add 10 mL $MgC1_2$ 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.

6.1.5 Heat at a rate that provides 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.

6.1.6 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.

6.1.7 Refill the gas washer with NaOH and demineralized water, as in 6.1.3, 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.

6.2 Set up manifold (fig. 2).

6.3 Allow the colorimeter, recorder, and heating bath to warm up for 30 min or until the heating-bath temperature has stabilized at 155 °C. Cold water must be flowing through the condensing jacket of the distillation head when heating bath is operating.

6.4 Adjust the baseline to read zero scale divisions on the recorder with all reagents, but with demineralized water in the sample tube.

6.5 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. Each sample must be well mixed by vigorous shaking before transferring a portion to a sample cup.

6.6 Begin analysis. When the peak from the most concentrated working standard appears on the recorder, adjust the STD 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 cyanide concentration.

7.2 Compute the concentration of dissolved or total recoverable cyanide in milligrams per liter by comparing each sample peak height with the analytical curve. Any baseline drift that may occur must be taken into account when computing the height of a sample or standard peak.

7.3 To determine milligrams per kilogram of cyanide in bottom-material samples, first determine the milligrams per liter of cyanide in each sample as in paragraph 7.2; then:

$$\text{CN(mg/kg)}= \frac{\text{mL distillate}}{\text{wt of sample (g)}} \text{ X mg/L CN}$$

8. Report

8.1 Report cyanide, dissolved (00723) and total-recoverable (00720), concentrations as follows: less than 1.00 mg/L, nearest 0.01 mg/L; 1.00 mg/L and above, two significant figures.

8.2 Report cyanide, total-recoverable-inbottom-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

9.1 Precision for dissolved cyanide expressed in terms of the percent relative standard deviation for replicate analysis by a single operator is as follows:

Mean (mg/L)	Relative Standard Deviation (percent)
0.041	2
0.125	1
0.224	1

9.2 It is estimated that the percent relative standard deviation for total recoverable cyanide

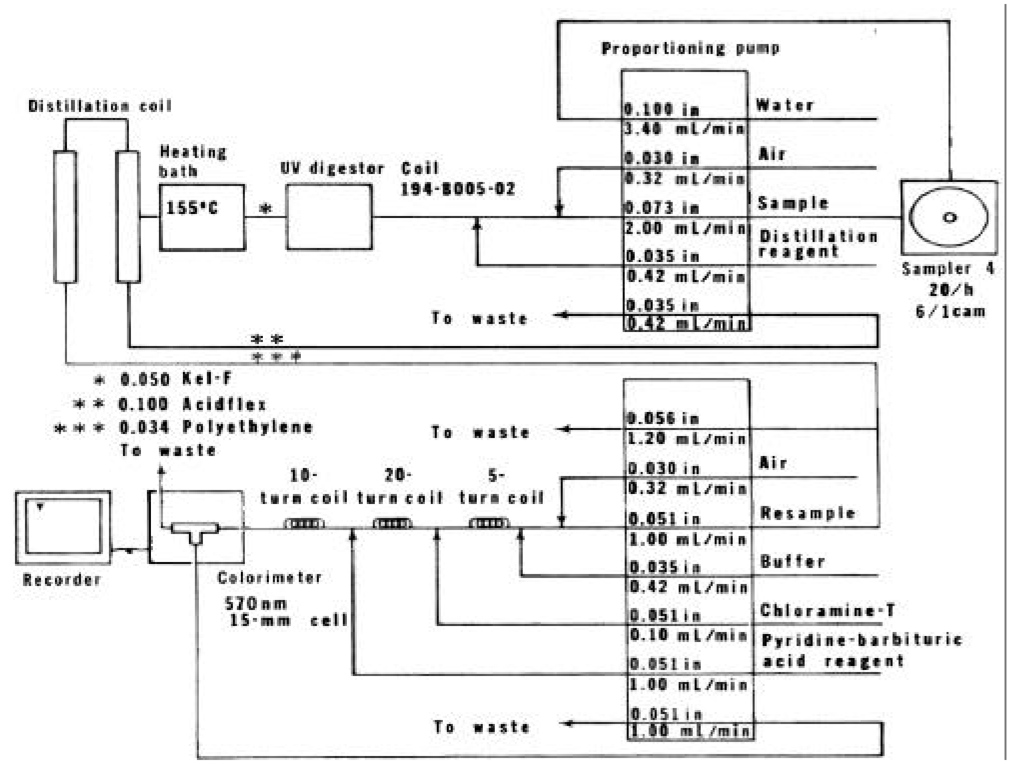

Figure 2. - Cyanide, barbituric acid mainfold

and for recoverable cyanide in bottom material will be greater than that reported for dissolved cyanide.

References

Goulden, P. D., Afghan, B. K., and Brooksbank, Peter, 1972, Determination of nanogram quantities of simple and complex cyanides in water: Analytical Chemistry, v. 44, p. 1845-49.

U.S. Environmental Protection Agency, 1979, Methods for chemical analysis of water and wastes: Cincinnati, p. 353.3-1.