

# Standard Methods for the Examination of Water and Wastewater

## 4500-CN<sup>-</sup> C. Total Cyanide after Distillation

### 1. General Discussion

Hydrogen cyanide (HCN) is liberated from an acidified sample by distillation and purging with air. The HCN gas is collected by passing it through an NaOH scrubbing solution. Cyanide concentration in the scrubbing solution is determined by titrimetric, colorimetric, or potentiometric procedures.

### 2. Apparatus

The apparatus is shown in Figure 4500-CN<sup>-</sup>:1. It includes:

- a. *Boiling flask*, 1 L, with inlet tube and provision for water-cooled condenser.
- b. *Gas absorber*, with gas dispersion tube equipped with medium-porosity fritted outlet.
- c. *Heating element*, adjustable.
- d. *Ground glass ST joints*, TFE-sleeved or with an appropriate lubricant for the boiling flask and condenser. Neoprene stopper and plastic threaded joints also may be used.

### 3. Reagents

- a. *Sodium hydroxide solution*: Dissolve 40 g NaOH in water and dilute to 1 L.
- b. *Magnesium chloride reagent*: Dissolve 510 g MgCl<sub>2</sub>·6H<sub>2</sub>O in water and dilute to 1 L.
- c. *Sulfuric acid*, H<sub>2</sub>SO<sub>4</sub>, 1 + 1.
- d. *Lead carbonate*, PbCO<sub>3</sub>, powdered.
- e. *Sulfamic acid*, NH<sub>2</sub>SO<sub>3</sub>H.

### 4. Procedure

a. Add 500 mL sample, containing not more than 10 mg CN<sup>-</sup>/L (diluted if necessary with distilled water) to the boiling flask. If a higher CN<sup>-</sup> content is anticipated, use the spot test (4500-CN<sup>-</sup>.K) to approximate the required dilution. Add 10 mL NaOH solution to the gas scrubber and dilute, if necessary, with distilled water to obtain an adequate liquid depth in the absorber. Do not use more than 225 mL total volume of absorber solution. When S<sup>2-</sup> generation from the distilling flask is anticipated add 50 or more mg powdered PbCO<sub>3</sub> to the absorber solution to precipitate S<sup>2-</sup>. Connect the train, consisting of boiling flask air inlet, flask, condenser, gas washer, suction flask trap, and aspirator. Adjust suction so that approximately 1 air bubble/s enters the boiling flask. This air rate will carry HCN gas from flask to absorber and usually will prevent a reverse flow of HCN through the air inlet. If this air rate does not prevent sample backup in the delivery tube, increase air-flow rate to 2 air bubbles/s. Observe air purge rate in the absorber where the liquid level should be raised not more than 6.5 to 10 mm. Maintain air flow throughout the reaction.

b. Add 2 g sulfamic acid through the air inlet tube and wash down with distilled water.

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c. Add 50 mL 1 M  $\text{H}_2\text{SO}_4$  through the air inlet tube. Rinse tube with distilled water and let air mix flask contents for 3 min. Add 20 mL  $\text{MgCl}_2$  reagent through air inlet and wash down with stream of water. A precipitate that may form redissolves on heating.

d. Heat with rapid boiling, but do not flood condenser inlet or permit vapors to rise more than halfway into condenser. Adequate refluxing is indicated by a reflux rate of 40 to 50 drops/min from the condenser lip. Reflux for at least 1 h. Discontinue heating but continue air flow for 15 min. Cool and quantitatively transfer absorption solution to a 250-mL volumetric flask. Rinse absorber and its connecting tubing sparingly with distilled water and add to flask. Dilute to volume with distilled water and mix thoroughly.

e. Determine cyanide concentration in the absorption solution by procedure of Section 4500-CN<sup>-</sup>.D, Section 4500-CN<sup>-</sup>.E, or Section 4500-CN<sup>-</sup>.F.

f. Distillation gives quantitative recovery of even refractory cyanides such as iron complexes. To obtain complete recovery of cobaltcyanide use ultraviolet radiation pretreatment.<sup>1,2</sup> If incomplete recovery is suspected, distill again by refilling the gas washer with a fresh charge of NaOH solution and refluxing 1 h more. The cyanide from the second reflux, if any, will indicate completeness of recovery.

g. As a quality control measure, periodically test apparatus, reagents, and other potential variables in the concentration range of interest. As an example at least  $100 \pm 4\%$  recovery from 1 mg CN<sup>-</sup>/L standard should be obtained.

### 5. References

1. CASAPIERI, P., R. SCOTT & E.A. SIMPSON. 1970. The determination of cyanide ions in waters and effluents by an Auto Analyzer procedure. *Anal. Chim. Acta* 49:188.
2. GOULDEN, P.D., K.A. BADAR & P. BROOKSBANK. 1972. Determination of nanogram quantities of simple and complex cyanides in water. *Anal. Chem.* 44:1845.

## 4500-CN<sup>-</sup> E. Colorimetric Method

### 1. General Discussion

a. *Principle:* CN<sup>-</sup> in the alkaline distillate from preliminary treatment is converted to CNCl by reaction with chloramine-T at pH <8 without hydrolyzing to CNO<sup>-</sup>.<sup>1</sup> (CAUTION—CNCl is a toxic gas; avoid inhalation.) After the reaction is complete, CNCl forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color absorbance in aqueous solution is between 575 and 582 nm. To obtain colors of comparable intensity, have the same salt content in sample and standards.

b. *Interference:* All known interferences are eliminated or reduced to a minimum by distillation.

### 2. Apparatus

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*Colorimetric equipment:* One of the following is required:

- a. *Spectrophotometer*, for use at 578 nm, providing a light path of 10 mm or longer.
- b. *Filter photometer*, providing a light path of at least 10 mm and equipped with a red filter having maximum transmittance at 570 to 580 nm.

### 3. Reagents

a. *Chloramine-T solution:* Dissolve 1.0 g white, water-soluble powder in 100 mL water. Prepare weekly and store in refrigerator.

b. *Stock cyanide solution:* Dissolve approximately 1.6 g NaOH and 2.51 g KCN in 1 L distilled water. (CAUTION—KCN is highly toxic; avoid contact or inhalation.) Standardize against standard silver nitrate ( $\text{AgNO}_3$ ) titrant as described in Section 4500-CN-D.4, using 25 mL KCN solution. Check titer weekly because the solution gradually loses strength; 1 mL = 1 mg  $\text{CN}^-$ .

c. *Standard cyanide solution:* Based on the concentration determined for the KCN stock solution (§ 3b) calculate volume required (approximately 10 mL) to prepare 1 L of a 10  $\mu\text{g}$   $\text{CN}^-/\text{mL}$  solution. Dilute with the NaOH dilution solution. Dilute 10 mL of the 10  $\mu\text{g}$   $\text{CN}^-/\text{mL}$  solution to 100 mL with the NaOH dilution solution; 1.0 mL = 1.0  $\mu\text{g}$   $\text{CN}^-$ . Prepare fresh daily and keep in a glass-stoppered bottle. (CAUTION—Toxic; take care to avoid ingestion.)

d. *Pyridine-barbituric acid reagent:* Place 15 g barbituric acid in a 250-mL volumetric flask and add just enough water to wash sides of flask and wet barbituric acid. Add 75 mL pyridine and mix. Add 15 mL conc hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to volume and mix until barbituric acid is dissolved. The solution is stable for approximately 6 months if stored in an amber bottle under refrigeration; discard if precipitate develops.

e. *Acetate buffer:* Dissolve 410 g sodium acetate trihydrate,  $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ , in 500 mL of water. Add glacial acetic acid to adjust to pH 4.5, approximately 500 mL.

f. *Sodium hydroxide dilution solution:* Dissolve 1.6 g NaOH in 1 L distilled water.

### 4. Procedure

a. *Preparation of standard curve:* Pipet a series of standards containing 1 to 10  $\mu\text{g}$   $\text{CN}^-$  into 50-mL volumetric flasks (0.02 to 0.2  $\mu\text{g}$   $\text{CN}^-/\text{mL}$ ). Dilute to 40 mL with NaOH dilution solution. Use 40 mL of NaOH dilution solution as blank. Develop and measure absorbance in 10-mm cells as described in § b for both standards and blank. For concentrations lower than 0.02  $\mu\text{g}$   $\text{CN}^-/\text{mL}$  use 100-mm cells.

Recheck calibration curve periodically and each time a new reagent is prepared.

b. *Color development:* Pipet a portion of absorption solution into a 50-mL volumetric flask and dilute to 40 mL with NaOH dilution solution. Add 1 mL acetate buffer and 2 mL chloramine-T solution, stopper, and mix by inversion twice. Let stand exactly 2 min.

Add 5 mL pyridine-barbituric acid reagent, dilute to volume with distilled water, mix

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thoroughly, and let stand exactly 8 min. Measure absorbance against distilled water at 578 nm.

Measure absorbance of blank (0.0 mg CN<sup>-</sup>/L) using 40 mL NaOH dilution solution and procedures for color development.

### 5. Calculation

Use the linear regression feature available on most scientific calculators, or compute slope and intercept of standard curve as follows:

$$m = \frac{n \sum ca - \sum c \sum a}{n \sum a^2 - (\sum a)^2}$$
$$b = \frac{\sum a^2 \sum c - \sum a \sum ac}{n \sum a^2 - (\sum a)^2}$$

where:

- $a$  = absorbance of standard solution,
- $c$  = concentration of CN<sup>-</sup> in standard, mg/L,
- $n$  = number of standard solutions,
- $m$  = slope of standard curve, and
- $b$  = intercept on  $c$  axis.

Include the blank concentration, 0.0 mg CN<sup>-</sup>/L and blank absorbance in the calculations above.

$$\text{CN}^-, \text{ mg/L} = (ma_1 + b) \times \frac{50}{X} \times \frac{250}{Y}$$

where:

- $X$  = absorption solution, mL,
- $Y$  = original sample, mL, and
- $a_1$  = absorbance of sample solution.

### 6. Precision and Bias<sup>2</sup>

Based on the results of nine operators in nine laboratories, the overall and single-operator precision of this method within its designated ranges may be expressed as follows:

$$\text{Reagent water: } S_T = 0.06x + 0.003$$
$$S_o = 0.11x + 0.010$$

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Selected water matrices:  $S_T = 0.04x + 0.018$

$$S_o = 0.04x + 0.008$$

where:

$S_T$  = overall precision, mg/L,

$S_o$  = single-operator precision, mg/L, and

$x$  = cyanide concentration, mg/L.

Recoveries of known amounts of cyanide from reagent water and selected water matrices (coke plant and refinery wastes, sewage, and surface water) are:

Medium	Added mg/L	Recovered mg/L	$n$	$S_T$	Bias	% Bias
Reagent	0.060	0.060	26	0.0101	0.000	0
water	0.500	0.480	23	0.0258	-0.020	-4
	0.900	0.996	27	0.0669	0.096	11
Selected	0.060	0.060	25	0.0145	0.000	0
water	0.500	0.489	26	0.0501	-0.011	-3
matrices	0.900	0.959	24	0.0509	0.059	7

## 7. References

1. AMUS, E. & H. GARSCHAGEN. 1953. Über die Verwendung der Barbitsäure für die photometrische Bestimmung von Cyanid und Rhodanid. *Z. Anal. Chem.* 138:414.
2. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1131. American Soc. Testing & Materials, Philadelphia, Pa.