Standard Methods for the Examination of Water and Wastewater

4500-CN^- CYANIDE*#(1)

4500-CN^- A. Introduction

1. General Discussion

''Cyanide'' refers to all of the CN groups in cyanide compounds that can be determined as the cyanide ion, CN^-, by the methods used. The cyanide compounds in which cyanide can be obtained as CN^- are classed as simple and complex cyanides.

Simple cyanides are represented by the formula $A(CN)_x$, where A is an alkali (sodium, potassium, ammonium) or a metal, and x, the valence of A, is the number of CN groups. In aqueous solutions of simple alkali cyanides, the CN group is present as CN^- and molecular HCN, the ratio depending on pH and the dissociation constant for molecular HCN (pK_a ~ 9.2). In most natural waters HCN greatly predominates.[1] In solutions of simple metal cyanides, the CN group may occur also in the form of complex metal-cyanide anions of varying stability. Many simple metal cyanides are sparingly soluble or almost insoluble [CuCN, AgCN, $Zn(CN)_2$], but they form a variety of highly soluble, complex metal cyanides in the presence of alkali cyanides.

Complex cyanides have a variety of formulae, but the alkali-metallic cyanides normally can be represented by $A_yM(CN)_x$. In this formula, A represents the alkali present y times, M the heavy metal (ferrous and ferric iron, cadmium, copper, nickel, silver, zinc, or others), and x the number of CN groups; x is equal to the valence of A taken y times plus that of the heavy metal. Initial dissociation of each of these soluble, alkali-metallic, complex cyanides yields an anion that is the radical $M(CN)_x^{y-}$. This may dissociate further, depending on several factors, with the liberation of CN^- and consequent formation of HCN.

The great toxicity to aquatic life of molecular HCN is well known;[2-5] it is formed in solutions of cyanide by hydrolytic reaction of CN^- with water. The toxicity of CN^- is less than that of HCN; it usually is unimportant because most of the free cyanide (CN group present as CN^- or as HCN) exists as HCN,[2-5] as the pH of most natural waters is substantially lower than the pK_a for molecular HCN. The toxicity to fish of most tested solutions of complex cyanides is attributable mainly to the HCN resulting from dissociation of the complexes.[2,4,5] Analytical distinction between HCN and other cyanide species in solutions of complex cyanides is possible.[2,5-9,10]

The degree of dissociation of the various metallocyanide complexes at equilibrium, which may not be attained for a long time, increases with decreased concentration and decreased pH, and is inversely related to the highly variable stability of the complexes.[2,4,5] The zinc- and cadmium-cyanide complexes are dissociated almost totally in very dilute solutions; thus these complexes can result in acute toxicity to fish at any ordinary pH. In equally dilute

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solutions there is much less dissociation for the nickel-cyanide complex and the more stable cyanide complexes formed with copper (I) and silver. Acute toxicity to fish from dilute solutions containing copper-cyanide or silver-cyanide complex anions can be due to the toxicity of the undissociated ions, although the complex ions are much less toxic than HCN.[2,5]

The iron-cyanide complex ions are very stable and not materially toxic; in the dark, acutely toxic levels of HCN are attained only in solutions that are not very dilute and have been aged for a long time. However, these complexes are subject to extensive and rapid photolysis, yielding toxic HCN, on exposure of dilute solutions to direct sunlight.[2,11] The photodecomposition depends on exposure to ultraviolet radiation, and therefore is slow in deep, turbid, or shaded receiving waters. Loss of HCN to the atmosphere and its bacterial and chemical destruction concurrent with its production tend to prevent increases of HCN concentrations to harmful levels. Regulatory distinction between cyanide complexed with iron and that bound in less stable complexes, as well as between the complexed cyanide and free cyanide or HCN, can, therefore, be justified.

Historically, the generally accepted physicochemical technique for industrial waste treatment of cyanide compounds is alkaline chlorination:

$$NaCN + Cl_2 \rightarrow CNCl + NaCl \qquad (1)$$

The first reaction product on chlorination is cyanogen chloride (CNCl), a highly toxic gas of limited solubility. The toxicity of CNCl may exceed that of equal concentrations of cyanide.[2,3,12] At an alkaline pH, CNCl hydrolyzes to the cyanate ion (CNO^-), which has only limited toxicity.

There is no known natural reduction reaction that may convert CNO^- to CN^-.[13] On the other hand, breakdown of toxic CNCl is pH- and time-dependent. At pH 9, with no excess chlorine present, CNCl may persist for 24 h.[14,15]

$$CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O \qquad (2)$$

CNO^- can be oxidized further with chlorine at a nearly neutral pH to CO_2 and N_2:

$$2NaCNO + 4NaOH + 3Cl_2 \rightarrow 6NaCl + 2CO_2 + N_2 + 2H_2O \qquad (3)$$

CNO^- also will be converted on acidification to NH_4^+:

$$2NaCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2NaHCO_3 \qquad (4)$$

The alkaline chlorination of cyanide compounds is relatively fast, but depends equally on the dissociation constant, which also governs toxicity. Metal cyanide complexes, such as nickel, cobalt, silver, and gold, do not dissociate readily. The chlorination reaction therefore requires more time and a significant chlorine excess.[16] Iron cyanides, because they do not dissociate to any degree, are not oxidized by chlorination. There is correlation between the

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refractory properties of the noted complexes, in their resistance to chlorination and lack of toxicity.

Thus, it is advantageous to differentiate between *total cyanide* and *cyanides amenable to chlorination*. When total cyanide is determined, the almost nondissociable cyanides, as well as cyanide bound in complexes that are readily dissociable and complexes of intermediate stability, are measured. Cyanide compounds that are amenable to chlorination include free cyanide as well as those complex cyanides that are potentially dissociable, almost wholly or in large degree, and therefore, potentially toxic at low concentrations, even in the dark. The chlorination test procedure is carried out under rigorous conditions appropriate for measurement of the more dissociable forms of cyanide.

The free and potentially dissociable cyanides also may be estimated when using the *weak acid dissociable* procedure. These methods depend on a rigorous distillation, but the solution is only slightly acidified, and elimination of iron cyanides is insured by the earlier addition of precipitation chemicals to the distillation flask and by the avoidance of ultraviolet irradiation.

The *cyanogen chloride* procedure is common with the colorimetric test for cyanides amenable to chlorination. This test is based on the addition of chloramine-T and subsequent color complex formation with pyridine-barbituric acid solution. Without the addition of chloramine-T, only existing CNCl is measured. CNCl is a gas that hydrolyzes to CNO^-; sample preservation is not possible. Because of this, spot testing of CNCl levels may be best. This procedure can be adapted and used when the sample is collected.

There may be analytical requirements for the determination of CNO^-, even though the reported toxicity level is low. On acidification, CNO^- decomposes to ammonia (NH_3).[3] Molecular ammonia and metal-ammonia complexes are toxic to aquatic life.[17]

Thiocyanate (SCN^-) is not very toxic to aquatic life.[2,18] However, upon chlorination, toxic CNCl is formed, as discussed above.[2,3,12] At least where subsequent chlorination is anticipated, the determination of SCN^- is desirable. Thiocyanate is biodegradable; ammonium is released in this reaction. Although the typical detoxifying agents used in cyanide poisoning induce thiocyanate formation, biochemical cyclic reactions with cyanide are possible, resulting in detectable levels of cyanide from exposure to thiocyanate.[18] Thiocyanate may be analyzed in samples properly preserved for determination of cyanide; however, thiocyanate also can be preserved in samples by acidification with H_2SO_4 to pH ≤2.

2. Cyanide in Solid Waste

a. Soluble cyanide: Determination of soluble cyanide requires sample leaching with distilled water until solubility equilibrium is established. One hour of stirring in distilled water should be satisfactory. Cyanide analysis is then performed on the leachate. Low cyanide concentration in the leachate may indicate presence of sparingly soluble metal cyanides. The cyanide content of the leachate is indicative of residual solubility of insoluble metal cyanides in the waste.

High levels of cyanide in the leachate indicate soluble cyanide in the solid waste. When 500 mL distilled water are stirred into a 500-mg solid waste sample, the cyanide

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concentration (mg/L) of the leachate multiplied by 1000 will give the solubility level of the cyanide in the solid waste in milligrams per kilogram. The leachate may be analyzed for total cyanide and/or cyanide amenable to chlorination.

b. Insoluble cyanide: The insoluble cyanide of the solid waste can be determined with the total cyanide method by placing a 500-mg sample with 500 mL distilled water in the distillation flask and in general following the distillation procedure (Section 4500-CN^-.C). In calculating, multiply by 1000 to give the cyanide content of the solid sample in milligrams per kilogram. Insoluble iron cyanides in the solid can be leached out earlier by stirring a weighed sample for 12 to 16 h in a 10% NaOH solution. The leached and wash waters of the solid waste will give the iron cyanide content with the distillation procedure. Prechlorination will have eliminated all cyanide amenable to chlorination. Do not expose sample to sunlight.

3. Selection of Method

a. Total cyanide after distillation: After removal of interfering substances, the metal cyanide is converted to HCN gas, which is distilled and absorbed in sodium hydroxide (NaOH) solution.[19] Because of the catalytic decomposition of cyanide in the presence of cobalt at high temperature in a strong acid solution,[20,21] cobalticyanide is not recovered completely. Indications are that cyanide complexes of the noble metals, i.e., gold, platinum, and palladium, are not recovered fully by this procedure either. Distillation also separates cyanide from other color-producing and possibly interfering organic or inorganic contaminants. Subsequent analysis is for the simple salt, sodium cyanide (NaCN). Some organic cyanide compounds, such as cyanohydrins, are decomposed by the distillation. Aldehydes convert cyanide to cyanohydrins.

The absorption liquid is analyzed by a titrimetric, colorimetric, or cyanide-ion-selective electrode procedure:

1) The titration method (D) is suitable for cyanide concentrations above 1 mg/L.

2) The colorimetric methods (E, N, and O) are suitable for cyanide concentrations as low as 1 to 5 μg/L under ideal conditions. Method N uses flow injection analysis of the distillate. Method O uses flow injection analysis following transfer through a semipermeable membrane for separating gaseous cyanide, and colorimetric analysis. Method E uses conventional colorimetric analysis of the distillate from Method C.

3) The ion-selective electrode method (F) using the cyanide ion electrode is applicable in the concentration range of 0.05 to 10 mg/L.

b. Cyanide amenable to chlorination:

1) Distillation of two samples is required, one that has been chlorinated to destroy all amenable cyanide present and the other unchlorinated. Analyze absorption liquids from both tests for total cyanide. The observed difference equals cyanides amenable to chlorination.

2) The colorimetric methods, by conversion of amenable cyanide and SCN^- to CNCl and developing the color complex with pyridine-barbituric acid solution, are used for the determination of the total of these cyanides (H, N, and O). Repeating the test with the cyanide masked by the addition of formaldehyde provides a measure of the SCN^- content.

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When subtracted from the earlier results this provides an estimate of the amenable CN^- content. This method is useful for natural and ground waters, clean metal finishing, and heat treating effluents. Sanitary wastes may exhibit interference.

3) The *weak acid dissociable cyanides* procedure also measures the cyanide amenable to chlorination by freeing HCN from the dissociable cyanide. After being collected in a NaOH absorption solution, CN^- may be determined by one of the finishing procedures given for the total cyanide determination. An automated procedure (O) also is presented.

It should be noted that although cyanide amenable to chlorination and weak acid dissociable cyanide appear to be identical, certain industrial effluents (e.g., pulp and paper, petroleum refining industry effluents) contain some poorly understood substances that may produce interference. Application of the procedure for cyanide amenable to chlorination yields negative values. For natural waters and metal-finishing effluents, the direct colorimetric determination appears to be the simplest and most economical.

c. Cyanogen chloride: The colorimetric method for measuring cyanide amenable to chlorination may be used, but omit the chloramine-T addition. The spot test also may be used.

d. Spot test for sample screening: This procedure allows a quick sample screening to establish whether more than 50 µg/L cyanide amenable to chlorination is present. The test also may be used to estimate the CNCl content at the time of sampling.

e. Cyanate: CNO^- is converted to ammonium carbonate, $(NH_4)_2CO_3$, by acid hydrolysis at elevated temperature. Ammonia (NH_3) is determined before the conversion of the CNO^- and again afterwards. The CNO^- is estimated from the difference in NH_3 found in the two tests. [22-24] Measure NH_3 by either:

1) The selective electrode method, using the NH_3 gas electrode (Section 4500-NH_3.D); or

2) The colorimetric method, using the phenate method for NH_3 (Section 4500-NH_3.F or Section 4500-NH_3.G).

f. Thiocyanate: Use the colorimetric determination with ferric nitrate as a color-producing compound.

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4500-CN^- B. Preliminary Treatment of Samples

CAUTION—*Use care in manipulating cyanide-containing samples because of toxicity. Process in a hood or other well-ventilated area. Avoid contact, inhalation, or ingestion.*

1. General Discussion

The nature of the preliminary treatment will vary according to the interfering substance present. Sulfides, fatty acids, and oxidizing agents are removed by special procedures. Most other interfering substances are removed by distillation. The importance of the distillation procedure cannot be overemphasized.

2. Preservation of Samples

Oxidizing agents, such as chlorine, decompose most cyanides. Test by placing a drop of sample on a strip of potassium iodide (KI)-starch paper previously moistened with acetate buffer solution, pH 4 (Section 4500-Cl.C.3*e*). If a bluish discoloration is noted, add 0.1 g sodium arsenite ($NaAsO_2$)/L sample and retest. Repeat addition if necessary. Sodium thiosulfate or ascorbic acid also may be used, but avoid an excess greater than 0.1 g $Na_2S_2O_3$/ L. Manganese dioxide, nitrosyl chloride, etc., if present, also may cause discoloration of the test paper. If possible, carry out this procedure before preserving sample as described below. If the following test indicates presence of sulfide, oxidizing compounds would not be expected.

Oxidized products of sulfide convert CN^- to SCN^- rapidly, especially at high pH.[1] Test for S^{2-} by placing a drop of sample on lead acetate test paper previously moistened with acetic acid buffer solution, pH 4 (Section 4500-Cl.C.3*e*). Darkening of the paper indicates presence of S^{2-}. Add lead acetate, or if the S^{2-} concentration is too high, add powdered lead carbonate [$Pb(CO_3)_2$] to avoid significantly reducing pH. Repeat test until a drop of treated sample no longer darkens the acidified lead acetate test paper. Filter sample before raising pH for stabilization. When particulate, metal cyanide complexes are suspected, filter solution before removing S^{2-}. Reconstitute sample by returning filtered particulates to the sample bottle after S^{2-} removal. Homogenize particulates before analyses.

Aldehydes convert cyanide to cyanohydrin. Longer contact times between cyanide and the aldehyde and the higher ratios of aldehyde to cyanide both result in increasing losses of cyanide that are not reversible during analysis. If the presence of aldehydes is suspected, stabilize with NaOH at time of collection and add 2 mL 3.5% ethylenediamine solution per 100 mL of sample.

Because most cyanides are very reactive and unstable, analyze samples as soon as possible. If sample cannot be analyzed immediately, add NaOH pellets or a strong NaOH

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solution to raise sample pH to 12 to 12.5, add dechlorinating agent if sample is disinfected, and store in a closed, dark bottle in a cool place.

To analyze for CNCl collect a separate sample and omit NaOH addition because CNCl is converted rapidly to CNO^- at high pH. Make colorimetric estimation immediately after sampling.

3. Interferences

a. Oxidizing agents may destroy most of the cyanide during storage and manipulation. Add $NaAsO_2$ or $Na_2S_2O_3$ as directed above; avoid excess $Na_2S_2O_3$.

b. Sulfide will distill over with cyanide and, therefore, adversely affect colorimetric, titrimetric, and electrode procedures. Test for and remove S^{2-} as directed above. Treat 25 mL more than required for the distillation to provide sufficient filtrate volume.

c. Fatty acids that distill and form soaps under alkaline titration conditions make the end point almost impossible to detect. Remove fatty acids by extraction.[2] Acidify sample with acetic acid (1 + 9) to pH 6.0 to 7.0. (CAUTION—*Perform this operation in a hood as quickly as possible.*) Immediately extract with iso-octane, hexane, or $CHCl_3$ (preference in order named). Use a solvent volume equal to 20% of sample volume. One extraction usually is adequate to reduce fatty acid concentration below the interference level. Avoid multiple extractions or a long contact time at low pH to minimize loss of HCN. When extraction is completed, immediately raise pH to >12 with NaOH solution.

d. Carbonate in high concentration may affect the distillation procedure by causing the violent release of carbon dioxide with excessive foaming when acid is added before distillation and by reducing pH of the absorption solution. Use calcium hydroxide to preserve such samples.[3] Add calcium hydroxide slowly, with stirring, to pH 12 to 12.5. After precipitate settles, decant supernatant liquid for determining cyanide.

Insoluble complex cyanide compounds will not be determined. If such compounds are present, filter a measured amount of well-mixed treated sample through a glass fiber or membrane filter (47-mm diam or less). Rinse filter with dilute (1 to 9) acetic acid until effervescence ceases. Treat entire filter with insoluble material as insoluble cyanide (Section 4500-CN^-.A.2*b*) or add to filtrate before distillation.

e. Other possible interferences include substances that might contribute color or turbidity. In most cases, distillation will remove these.

Note, however, that the strong acid distillation procedure requires using sulfuric acid with various reagents. With certain wastes, these conditions may result in reactions that otherwise would not occur in the aqueous sample. As a quality control measure, periodically conduct addition and recovery tests with industrial waste samples.

f. Aldehydes convert cyanide to cyanohydrin, which forms nitrile under the distillation conditions. Only direct titration without distillation can be used, which reveals only non-complex cyanides. Formaldehyde interference is noticeable in concentrations exceeding 0.5 mg/L. Use the following spot test to establish absence or presence of aldehydes (detection limit 0.05 mg/L):[4-6]

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1) Reagents

a) *MBTH indicator solution:* Dissolve 0.05 g 3-methyl, 2-benzothiazolone hydrazone hydrochloride in 100 mL water. Filter if turbid.

b) *Ferric chloride oxidizing solution:* Dissolve 1.6 g sulfamic acid and 1 g $FeCl_3 \cdot 6H_2O$ in 100 mL water.

c) *Ethylenediamine solution,* 3.5%: Dilute 3.5 mL pharmaceutical-grade anhydrous $NH_2CH_2CH_2NH_2$ to 100 mL with water.

2) Procedure—If the sample is alkaline, add 1 + 1 H_2SO_4 to 10 mL sample to adjust pH to less than 8. Place 1 drop of sample and 1 drop distilled water for a blank in separate cavities of a white spot plate. Add 1 drop MBTH solution and then 1 drop $FeCl_3$ oxidizing solution to each spot. Allow 10 min for color development. The color change will be from a faint green-yellow to a deeper green with blue-green to blue at higher concentrations of aldehyde. The blank should remain yellow.

To minimize aldehyde interference, add 2 mL of 3.5% ethylenediamine solution/100 mL sample. This quantity overcomes the interference caused by up to 50 mg/L formaldehyde.

When using a known addition in testing, 100% recovery of the CN^- is not necessarily to be expected. Recovery depends on the aldehyde excess, time of contact, and sample temperature.

g. Glucose and other sugars, especially at the pH of preservation, lead to cyanohydrin formation by reaction of cyanide with aldose.[7] Reduce cyanohydrin to cyanide with ethylenediamine (see above). MBTH is not applicable.

h. Nitrite may form HCN during distillation in Methods C, G, and L, by reacting with organic compounds.[8,9] Also, NO_3^- may reduce to NO_2^-, which interferes. To avoid NO_2^- interference, add 2 g sulfamic acid to the sample before distillation. *Nitrate* also may interfere by reacting with SCN^-.[10]

i. Some sulfur compounds may decompose during distillation, releasing S, H_2S, or SO_2. Sulfur compounds may convert cyanide to thiocyanate and also may interfere with the analytical procedures for CN^-. To avoid this potential interference, add 50 mg $PbCO_3$ to the absorption solution before distillation. Filter sample before proceeding with the colorimetric or titrimetric determination.

Absorbed SO_2 forms Na_2SO_3 which consumes chloramine-T added in the colorimetric determination. The volume of chloramine-T added is sufficient to overcome 100 to 200 mg SO_3^{2-}/L. Test for presence of chloramine-T after adding it by placing a drop of sample on KI-starch test paper; add more chloramine-T if the test paper remains blank, or use Method F.

Some wastewaters, such as those from coal gasification or chemical extraction mining, contain high concentrations of sulfites. Pretreat sample to avoid overloading the absorption solution with SO_3^{2-}. Titrate a suitable sample iodometrically (Section 4500-O) with dropwise addition of 30% H_2O_2 solution to determine volume of H_2O_2 needed for the 500

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mL distillation sample. Subsequently, add H_2O_2 dropwise while stirring, but in only such volume that not more than 300 to 400 mg SO_3^{2-}/L will remain. Adding a lesser quantity than calculated is required to avoid oxidizing any CN^- that may be present.

j. Alternate procedure: The strong acid distillation procedure uses concentrated acid with magnesium chloride to dissociate metal-cyanide complexes. In some instances, particularly with industrial wastes, it may be susceptible to interferences such as those from conversion of thiocyanate to cyanide in the presence of an oxidant, e.g., nitrate. If such interferences are present use a ligand displacement procedure with a mildly acidic medium with EDTA to dissociate metal-cyanide complexes.[10] Under such conditions thiocyanate is relatively stable and many oxidants, including nitrate, are weaker.

If any cyanide procedure is revised to meet specific requirements, obtain recovery data by the addition of known amounts of cyanide.

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4500-CN^- 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^-: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 $MgCl_2 \cdot 6H_2O$ in water and dilute to 1 L.

c. Sulfuric acid, H_2SO_4, 1 + 1.

d. Lead carbonate, $PbCO_3$, powdered.

e. Sulfamic acid, NH_2SO_3H.

4. Procedure

a. Add 500 mL sample, containing not more than 10 mg CN^-/ L (diluted if necessary with distilled water) to the boiling flask. If a higher CN^- content is anticipated, use the spot test (4500-CN^-.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^{2-} generation from the distilling flask is anticipated add 50 or more mg powdered $PbCO_3$ to the absorber solution to precipitate S^{2-}. 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 1 H_2SO_4 through the air inlet tube. Rinse tube with distilled water and let air mix flask contents for 3 min. Add 20 mL $MgCl_2$ 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^-.D, Section 4500-CN^-.E, or Section 4500-CN^-.F.

f. Distillation gives quantitative recovery of even refractory cyanides such as iron complexes. To obtain complete recovery of cobalticyanide use ultraviolet radiation pretreatment.[1,2] 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 ± 4% recovery from 1 mg CN^-/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^- D. Titrimetric Method

1. General Discussion

a. Principle: CN^- in the alkaline distillate from the preliminary treatment procedure is titrated with standard silver nitrate ($AgNO_3$) to form the soluble cyanide complex, $Ag(CN)_2^-$. As soon as all CN^- has been complexed and a small excess of Ag^+ has been added, the excess Ag^+ is detected by the silver-sensitive indicator, *p*-dimethylaminobenzalrhodanine, which immediately turns from a yellow to a salmon color.[1] The distillation has provided a 2:1 concentration. The indicator is sensitive to about 0.1 mg Ag/L. If titration shows that CN^- is below 1 mg/L, examine another portion colorimetrically or potentiometrically.

2. Apparatus

Koch microburet, 10-mL capacity.

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3. Reagents

a. Indicator solution: Dissolve 20 mg *p*-dimethylaminobenzalrhodanine in 100 mL acetone.

b. Standard silver nitrate titrant: Dissolve 3.27 g $AgNO_3$ in 1 L distilled water. Standardize against standard NaCl solution, using the argentometric method with K_2CrO_4 indicator, as directed in Chloride, Section 4500-Cl^-.B.

Dilute 500 mL $AgNO_3$ solution according to the titer found so that 1.00 mL is equivalent to 1.00 mg CN^-.

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

4. Procedure

a. From the absorption solution take a measured volume of sample so that the titration will require approximately 1 to 10 mL $AgNO_3$ titrant. Dilute to 100 mL using the NaOH dilution solution or to some other convenient volume to be used for all titrations. For samples with low cyanide concentration (≤5 mg/L) do not dilute. Add 0.5 mL indicator solution.

b. Titrate with standard $AgNO_3$ titrant to the first change in color from a canary yellow to a salmon hue. Titrate a blank containing the same amount of alkali and water, i.e., 100 mL NaOH dilution solution (or volume used for sample). As the analyst becomes accustomed to the end point, blank titrations decrease from the high values usually experienced in the first few trials to 1 drop or less, with a corresponding improvement in precision.

5. Calculation

$$\text{mg } CN^-/L = \frac{(A - B) \times 1000}{\text{mL original sample}} \times \frac{250}{\text{mL portion used}}$$

where:

A = mL standard $AgNO_3$ for sample and
B = mL standard $AgNO_3$ for blank.

6. Precision and Bias[2]

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

Reagent water: $S_T = 0.04x + 0.038$

$S_o = 0.01x + 0.018$

Selected water matrices: $S_T = 0.06x + 0.711$

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$$S_o = 0.04x + 0.027$$

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 are:

Medium	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
Reagent	2.00	2.10	18	0.1267	0.10	5
water	5.00	4.65	18	0.2199	–0.35	–7
	5.00	5.18	18	0.2612	0.18	4
Selected	2.00	2.80	18	0.8695	0.80	40
water	5.00	5.29	18	1.1160	0.29	6
matrices	5.00	5.75	18	0.9970	0.75	15

7. References

1. RYAN, J.A. & G.W. CULSHAW. 1944. The use of *p*-dimethylaminobenzylidene rhodanine as an indicator for the volumetric determination of cyanides. *Analyst* 69:370.
2. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1131. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- E. Colorimetric Method

1. General Discussion

a. Principle: CN^- in the alkaline distillate from preliminary treatment is converted to CNCl by reaction with chloramine-T at pH <8 without hydrolyzing to CNO^-.[1] (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.

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2. Apparatus

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 ($AgNO_3$) 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 CN^-.

c. Standard cyanide solution: Based on the concentration determined for the KCN stock solution (¶ 3*b*) calculate volume required (approximately 10 mL) to prepare 1 L of a 10 µg CN^-/ mL solution. Dilute with the NaOH dilution solution. Dilute 10 mL of the 10 µg CN^-/mL solution to 100 mL with the NaOH dilution solution; 1.0 mL = 1.0 µg 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, $NaC_2H_3O_2 \cdot 3H_2O$, 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 µg CN^- into 50-mL volumetric flasks (0.02 to 0.2 µg CN^-/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 µg CN^-/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.

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Add 5 mL pyridine-barbituric acid reagent, dilute to volume with distilled water, mix thoroughly, and let stand exactly 8 min. Measure absorbance against distilled water at 578 nm.

Measure absorbance of blank (0.0 mg CN^-/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^- 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^-/L and blank absorbance in the calculations above.

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

where:

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

6. Precision and Bias[2]

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:

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 Bestimmund 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.

4500-CN^- F. Cyanide-Selective Electrode Method

1. General Discussion

CN^- in the alkaline distillate from the preliminary treatment procedures can be determined potentiometrically by using a CN^--selective electrode in combination with a double-junction reference electrode and a pH meter having an expanded millivolt scale, or a specific ion meter. This method can be used to determine CN^- concentration in place of either the colorimetric or titrimetric procedures in the concentration range of 0.05 to 10 mg CN^-/L.[1-3] If the CN^--selective electrode method is used, the previously described titration screening step can be omitted.

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2. Apparatus

a. Expanded-scale pH meter or specific-ion meter.

b. Cyanide-ion-selective electrode.#(2)

c. Reference electrode, double-junction.

d. Magnetic mixer with TFE-coated stirring bar.

e. Koch microburet, 10-mL capacity.

3. Reagents

a. Stock standard cyanide solution: See Section 4500-CN^-.E.3*b*.

b. Sodium hydroxide dilution solution: Dissolve 1.6 g NaOH in water and dilute to 1 L.

c. Standard cyanide solution: Dilute a calculated volume (approximately 25 mL) of stock KCN solution, based on the determined concentration, to 1000 mL with NaOH diluent. Mix thoroughly; 1 mL 25 µg CN^-.

d. Dilute standard cyanide solution: Dilute 100.0 mL standard CN^- solution to 1000 mL with NaOH diluent; 1.00 mL = 2.5 µg CN^-. Prepare daily and keep in a dark, glass-stoppered bottle.

e. Potassium nitrate solution: Dissolve 100 g KNO_3 in water and dilute to 1 L. Adjust to pH 12 with KOH. This is the outer filling solution for the double-junction reference electrode.

4. Procedure

a. Calibration: Using Koch microburet and standard CN^- solution, prepare four (or more) additional solutions containing 2.5, 0.25, 0.125, and 0.025 µg CN^-/mL in NaOH dilution solution. Transfer approximately 100 mL of each of these standard solutions into a 250-mL beaker prerinsed with a small portion of standard being tested. Immerse CN^- and double-junction reference electrodes. Mix well on a magnetic stirrer at 25°C, maintaining as closely as possible the same stirring rate for all solutions.

Always progress from the lowest to the highest concentration of standard because otherwise equilibrium is reached only slowly. The electrode membrane dissolves in solutions of high CN^- concentration; do not use with a concentration above 25 µg CN^-/mL. After making measurements remove electrode and soak in water.

After equilibrium is reached (at least 5 min and not more than 10 min), record potential (millivolt) readings. Plot CN^- concentration on logarithmic axis of semilogarithmic paper versus potential developed in solution on linear axis. A straight line with a slope of approximately 59 mV per decade indicates that the instrument and electrodes are operating properly. Record slope of line obtained (millivolts/decade of concentration). The slope may vary somewhat from the theoretical value of 59.2 mV per decade because of manufacturing variation and reference electrode (liquid-junction) potentials. The slope should be a straight line and is the basis for calculating sample concentration. Follow manufacturer's instructions for direct-reading ion meters.

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b. Measurement of sample: Place 100 mL of absorption liquid obtained in Section 4500-CN^-.C.4*d* (or an accurately measured portion diluted to 100 mL with NaOH dilution solution) into a 250-mL beaker. When measuring low CN^- concentrations, first rinse beaker and electrodes with a small volume of sample. Immerse CN^- and double-junction reference electrodes and mix on a magnetic stirrer at the same stirring rate used for calibration. After equilibrium is reached (at least 5 min and not more than 10 min), record values indicated on ion meter or found from graph prepared as above. Calculate concentration as directed below.

5. Calculations

$$\text{mg } CN^-/L = \mu\text{g } CN^-/\text{mL from graph or meter} \times \frac{100}{x} \times \frac{250}{y}$$

where:

x = volume of absorption solution, mL, and
y = volume of original sample, mL.

6. Precision and Bias[4]

The precision of the CN^--ion-selective electrode method using the absorption solution from total cyanide distillation has been found in collaborative testing to be linear within its designated range.

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

Reagent water: $S_T = 0.06x + 0.003$
$S_o = 0.03x + 0.008$

Selected water matrices: $S_T = 0.05x + 0.008$
$S_o = 0.03x + 0.012$

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 are:

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are:

Medium	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
Reagent	0.060	0.059	18	0.0086	–0.001	2
water	0.500	0.459	18	0.0281	–0.041	–8
	0.900	0.911	18	0.0552	0.011	1
	5.00	5.07	18	0.297	0.07	1
Selected	0.060	0.058	14	0.0071	–0.002	–3
water	0.500	0.468	21	0.0414	–0.032	–6
matrices	0.900	0.922	19	0.0532	0.022	2
	5.00	5.13	20	0.2839	0.13	3

7. References

1. ORION RESEARCH, INC. 1975. Cyanide Ion Electrode Instruction Manual. Cambridge, Mass.
2. FRANT, M.S., J.W. ROSS & J.H. RISEMAN. 1972. An electrode indicator technique for measuring low levels of cyanide. *Anal. Chem.* 44:2227.
3. SEKERKA, J. & J.F. LECHNER. 1976. Potentiometric determination of low levels of simple and total cyanides. *Water Res.* 10:479.
4. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1131. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- G. Cyanides Amenable to Chlorination after Distillation

1. General Discussion

This method is applicable to the determination of cyanides amenable to chlorination.

After part of the sample is chlorinated to decompose the cyanides, both the chlorinated and the untreated sample are subjected to distillation as described in Section 4500-CN^-.C. The difference between the CN^- concentrations found in the two samples is expressed as cyanides amenable to chlorination.

Some unidentified organic chemicals may oxidize or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination. This may lead to a negative value for cyanides amenable to chlorination after distillation for wastes from, for example, the steel industry, petroleum refining, and pulp and paper processing. Where such interferences are encountered use Method Section 4500-CN^-.I for determining dissociable cyanide.

Protect sample from exposure to ultraviolet radiation, and perform manipulations under

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incandescent light, to prevent photodecomposition of some metal-cyanide complexes by ultraviolet light.

2. Apparatus

a. Distillation apparatus: See Section 4500-CN^-.C.2.

b. Apparatus for determining cyanide by either the titrimetric method, Section 4500-CN^-.D.2, the colorimetric method, Section 4500-CN^-.E.2, or the electrode method, Section 4500-CN^-.F.2.

3. Reagents

a. All reagents listed in Section 4500-CN^-.C.3.

b. All reagents listed in Section 4500-CN^-.D.3, Section 4500-CN^-.E.3, or Section 4500-CN^-.F.3, depending on method of estimation.

c. Calcium hypochlorite solution: Dissolve 5 g $Ca(OCl)_2$ in 100 mL distilled water. Store in an amber-colored glass bottle in the dark. Prepare monthly.

d. Potassium iodide(KI)-starch test paper.

4. Procedure

a. Divide sample into two equal portions of 500 mL (or equal portions diluted to 500 mL) and chlorinate one as in ¶ b below. Analyze both portions for CN^-. The difference in determined concentrations is the cyanide amenable to chlorination.

b. Place one portion in a 1-L beaker covered with aluminum foil or black paper. Keep beaker covered with a wrapped watch glass during chlorination. Add $Ca(OCl)_2$ solution dropwise to sample while agitating and maintaining pH between 11 and 12 by adding NaOH solution. Test for chlorine by placing a drop of treated sample on a strip of KI-starch paper. A distinct blue color indicates sufficient chlorine (approximately 50 to 100 mg Cl_2/L). Maintain excess residual chlorine for 1 h while agitating. If necessary, add more $Ca(OCl)_2$ and/or NaOH.

c. After 1 h remove any residual chlorine by dropwise addition of $NaAsO_2$ solution (2 g/100 mL) or by addition of 8 drops H_2O_2 (3%) followed by 4 drops $Na_2S_2O_3$ solution (500 g/L). Test with KI-starch paper until there is no color change.

d. Distill both chlorinated and unchlorinated samples as in Section 4500-CN^-.C. Test according to Methods D, E, or F.

5. Calculation

$$\text{mg } CN^- \text{ amenable to chlorination/L} = G - H$$

where:

G = mg CN^-/L found in unchlorinated portion of sample and
H = mg CN^-/L found in chlorinated portion of sample.

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For samples containing significant quantities of iron cyanides, it is possible that the second distillation will give a higher value for CN^- than the test for total cyanide, leading to a negative result. When the difference is within the precision limits of the method, report, ‘‘no determinable quantities of cyanide amenable to chlorination.’’ If the difference is greater than the precision limit, ascertain the cause such as presence of interferences, manipulation of the procedure, etc., or use Method I.

6. Precision and Bias[1]

The precision and bias information given in this section may not apply to waters of untested matrices.

a. Precision:

1) Colorimetric—Based on the results of eight operators in seven laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{Reagent water: } S_T = 0.18x + 0.005$$
$$S_o = 0.06x + 0.003$$

$$\text{Selected water matrices: } S_T = 0.20x + 0.009$$
$$S_o = 0.05x + 0.005$$

2) Titrimetric—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{Reagent water: } S_T = 0.01x + 0.439$$
$$S_o = 0.241 - 0.03x$$

$$\text{Selected water matrices: } S_T = 0.12x + 0.378$$
$$S_o = 0.209 - 0.01x$$

where:

S_T = overall precision, mg/L,
S_o = single-operator precision, mg/L, and
x = cyanide concentration, mg CN^-/L

b. Bias: Recoveries of known amount of cyanide amenable to chlorination from reagent water and selected water matrices are shown below:

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water and selected water matrices are shown below:

Medium	Technique	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
Reagent water	Colorimetric	0.008	0.009	21	0.0033	0.001	13
		0.019	0.023	20	0.0070	0.004	21
		0.080	0.103	20	0.0304	0.018	23
		0.191	0.228	21	0.0428	0.037	19
	Titrimetric	1.00	0.73	18	0.350	–0.27	–27
		1.00	0.81	18	0.551	–0.19	–19
		4.00	3.29	18	0.477	–0.71	–18
Selected water matrices	Colorimetric	0.008	0.013	17	0.0077	0.005	63
		0.019	0.025	18	0.0121	0.006	32
		0.080	0.100	18	0.0372	0.020	25
		0.191	0.229	18	0.0503	0.038	20
	Titrimetric	1.00	1.20	18	0.703	0.20	20
		1.00	1.10	18	0.328	0.10	10
		4.00	3.83	18	0.818	–0.17	–4

7. Reference

1. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1131. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- H. Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)

1. General Discussion

This method covers the determination of HCN and of CN complexes that are amenable to chlorination and also thiocyanates (SCN^-). The procedure does not measure cyanates (CNO^-) or iron cyanide complexes, but does determine cyanogen chloride (CNCl). It may be modified for use in presence of thiocyanates. The method requires neither lengthy distillation nor the chlorination of one sample before distillation. The recovery of CN^- from metal cyanide complexes will be comparable to that in Methods G and I.

The cyanides are converted to CNCl by chloramine-T after the sample has been heated. In the absence of nickel, copper, silver, and gold cyanide complexes or SCN^-, the CNCl may be developed at room temperature. The pyridine-barbituric acid reagent produces a red-blue color in the sample. The color can be estimated visually against standards or photometrically

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at 578 nm. The dissolved salt content in the standards used for the development of the calibration curve should be near the salt content of the sample, including the added NaOH and phosphate buffer.

The method's usefulness is limited by thiocyanate interference. Although the procedure allows the specific determination of CN^- amenable to chlorination (see Section 4500-CN^-.H.2 and Section 4500-CN^-.H.5) by masking the CN^- content and thereby establishing a correction for the thiocyanide content, the ratio of SCN^- to CN^- should not exceed 3 to be applicable. In working with unknown samples, screen the sample for SCN^- by the spot test (Section 4500-CN^-.K).

2. Interferences

a. Remove interfering agents as described in Section 4500-CN^-.B with the exception of NO_2^- and NO_3^- (Section 4500-CN^-.B.3*h*).

b. The SCN^- ion reacts with chloramine-T to give a positive error equivalent to its concentration. The procedure allows the separate determination of SCN^- and subtraction of this value from the results for the total. Use the spot test (Section 4500-CN^-.K) for SCN^- when its presence is suspected. If the SCN^- content is more than three times the CN^- content, use Method G or I.

c. Reducing chemical compounds, such as SO_3^{2-}, may interfere by consuming chlorine in the chloramine-T addition. A significant excess of chlorine is provided, but the procedure prescribes a test (Section 4500-CN^-.H.5*d*) to avoid this interference.

d. Color and turbidity may interfere with the colorimetric determination. Overcome this interference by extraction with chloroform (Section 4500-CN^-.B.3*c*) but omit reduction of the pH. Otherwise, use Method G or I.

Compensation for color and turbidity may be made by determining absorbance of a second sample solution to which all reagents except chloramine-T have been added.

e. Color intensity and absorption are affected by wide variations in total dissolved solids content of the sample.

For samples containing high concentrations of dissolved solids (3000 to 10 000 mg/L), add 6 g NaCl/L NaOH solution (1.6 g/L) used to prepare standards. For samples containing dissolved solids concentrations greater than 10 000 mg/L, add sufficient NaCl to the NaOH solution to approximate the dissolved solids content.

3. Apparatus

a. Apparatus listed in Section 4500-CN^-.E.2.

b. Hot water bath.

4. Reagents

a. Reagents listed in Section 4500-CN^-.B and Section 4500-CN^-.E.3.

b. Sodium chloride, NaCl, crystals.

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c. Sodium carbonate, Na_2CO_3, crystals.

d. Sulfuric acid solution, H_2SO_4, 1*N*.

e. EDTA solution, 0.05*M:* Dissolve 18.5 g disodium salt of ethylenediamine tetraacetic acid in water and dilute to 1 L.

f. Formaldehyde solution, 10%: Dilute 27 mL formaldehyde (37% pharmaceutical grade) to 100 mL.

g. Phosphate buffer: Dissolve 138 g sodium dihydrogen phosphate monohydrate, $NaH_2PO_4 \cdot H_2O$, in water and dilute to 1 L. Refrigerate.

5. Procedure

a. Calibrate as directed in Section 4500-CN^-.E.1*a* and Section 4500-CN^-.E.4*a*. For samples with more than 3000 mg total dissolved solids/L, prepare a calibration curve from standards and blank NaOH solutions containing 6 g NaCl/L. Samples containing total dissolved solids exceeding 10 000 mg/L require appropriate standards and a new calibration curve.

b. Adjust pH of 50 mL sample to between 11.4 and 11.8. If acid is needed, add a small amount (0.2 to 0.4 g) of sodium carbonate and stir to dissolve. Then add HCl solution (1+9) dropwise while stirring. For raising the pH, use NaOH solution (40 g/L).

c. Pipet 20.0 mL of adjusted sample into a 50-mL volumetric flask. If the cyanide concentration is greater than 0.3 mg/L, use a smaller portion and dilute to 20 mL with NaOH solution. Do not exceed the concentration limit of 0.3 mg/L.

d. To insure uniform color development, both in calibration and testing, maintain a uniform temperature. Immerse flasks in a water bath held at 27 ± 1°C for 10 min before adding reagents and keep samples in water bath until all reagents have been added.

Add 4 mL phosphate buffer and swirl to mix. Add one drop of EDTA solution, and mix.

e. Add 2 mL chloramine-T solution and swirl to mix. Place 1 drop of sample on potassium iodide-starch test paper that has been moistened previously with acetate buffer solution. Repeat the chloramine-T addition if required. After exactly 3 min, add 5 mL pyridine-barbituric acid reagent and swirl to mix.

f. Remove samples from water bath, dilute to volume, and mix. Allow 8 min from the addition of the pyridine-barbituric acid reagent for color development.

Determine absorbance at 578 nm in a 1.0-cm cell versus distilled water.

Calculate concentration of cyanide, mg/L in the original sample following instructions given in 4500-CN^- E.

g. If the presence of thiocyanate is suspected, pipet a second 20-mL portion of pH-adjusted sample into a 50-mL volumetric flask. Add 3 drops 10% formaldehyde solution. Mix and let stand 10 min. Place in a water bath at 27 ± 1°C for an additional 10 min before the addition of the reagent chemicals and hold in the bath until all reagents have been added.

Continue with *b* above.

Calculate the concentration of cyanide, as milligrams per liter, in the original sample

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following instructions given in Section 4500-CN^-.E.

h. In the presence of thiocyanate, cyanide amenable to chlorination is equal to the difference between the concentrations of cyanide obtained in and *g.*

6. Calculation

See Section 4500-CN^-.E.5.

Deduct SCN^- value from the results found when the CN^- has not been masked by formaldehyde addition (total) for cyanide content.

7. Precision and Bias[1]

This precision and bias information may not apply to waters of untested matrices.

a. Precision: Based on the results of 14 operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{Reagent water: } S_T = 0.10x + 0.006$$
$$S_o = 0.07x + 0.005$$

$$\text{Selected water matrices: } S_T = 0.11x + 0.007$$
$$S_o = 0.02x + 0.005$$

where:

S_T = overall precision, mg/L,
S_o = single-operator precision, mg/L, and
x = cyanide concentration, mg/L.

b. Bias: Recoveries of known amounts of cyanide from reagent water and selected water matrices including creek waters, diluted sewage (1 to 20), and industrial wastewater are shown below.

	Added mg/L		Recovered				
Medium	CN^-	SCN^-	mg/L	n	S_T	Bias	% Bias
Reagent	0.005		0.007	42	0.0049	0.002	40
water	0.027		0.036	41	0.0109	0.009	25
	0.090		0.100	42	0.0167	0.010	11
	0.090	0.080	0.080	39	0.0121	–0.010	11
	0.270		0.276	42	0.0320	0.006	2
Selected	0.005		0.003	40	0.0042	–0.002	40

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Medium	Added mg/L CN^-	Added mg/L SCN^-	Recovered mg/L	*n*	S_T	Bias	% Bias
water	0.027		0.026	42	0.0093	–0.001	4
matrices	0.090		0.087	42	0.0202	–0.003	3
	0.090	0.080	0.068	37	0.0146	–0.022	24
	0.270		0.245	41	0.0319	–0.025	9

8. Reference

1. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1074. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- I. Weak Acid Dissociable Cyanide

1. General Discussion

Hydrogen cyanide (HCN) is liberated from a slightly acidified (pH 4.5 to 6.0) sample under the prescribed distillation conditions. The method does not recover CN^- from tight complexes that would not be amenable to oxidation by chlorine. The acetate buffer used contains zinc salts to precipitate iron cyanide as a further assurance of the selectivity of the method. In other respects the method is similar to 4500-CN^-.C.

2. Interferences

See Section 4500-CN^-.B.3.

Protect sample and apparatus from ultraviolet light to prevent photodecomposition of some metal-cyanide complexes and an increase in concentration of weak acid dissociable cyanide.

If procedure is used to determine low concentrations of cyanide in samples of ferri- and ferrocyanide, add more, e.g., fivefold excess, zinc acetate solution before adding acid and distilling.

3. Apparatus

See Section 4500-CN^-.C.2 and Figure 4500-CN^-:1, and also Section 4500-CN^-.D.2, Section 4500-CN^-.E.2, or Section 4500-CN^-.F.2, depending on method of estimation.

4. Reagents

a. Reagents listed in Section 4500-CN^-.C.3.

b. Reagents listed in Section 4500-CN^-.D.3, Section 4500-CN^-.E.3, or Section 4500-CN^-.F.3, depending on method of estimation.

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c. Acetic acid, 1 + 9: Mix 1 volume of glacial acetic acid with 9 volumes of water.

d. Acetate buffer: Dissolve 410 g sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL water. Add glacial acetic acid to yield a solution pH of 4.5 (approximately 500 mL).

e. Zinc acetate solution, 100 g/L: Dissolve 120 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 500 mL water. Dilute to 1 L.

f. Methyl red indicator.

5. Procedure

Follow procedure described in Section 4500-CN^-.C.4, but with the following modifications:

a. Do not add sulfamic acid, because NO_2^- and NO_3^- do not interfere.

b. Instead of H_2SO_4 and $MgCl_2$ reagents, add 20 mL each of the acetate buffer and zinc acetate solutions through air inlet tube. Also add 2 to 3 drops methyl red indicator. Rinse air inlet tube with water and let air mix contents. If the solution is not pink, add acetic acid (1 + 9) dropwise through air inlet tube until a pink color persists.

c. Follow instructions beginning with Section 4500-CN^-.C.4*d*.

d. For determining CN^- in the absorption solution, use the preferred finish method (Section 4500-CN^-.D, Section 4500-CN^-.E, or Section 4500-CN^-.F).

6. Precision and Bias[1]

The precision and bias information given in this section may not apply to waters of untested matrices.

a. Precision:

1) Colorimetric—Based on the results of nine operators in nine laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{Reagent water: } S_T = 0.09x + 0.010$$
$$S_o = 0.08x + 0.005$$

$$\text{Selected water matrices: } S_T = 0.08x + 0.012$$
$$S_o = 0.05x + 0.008$$

2) Electrode—Based on the results of six operators in five laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

$$\text{Reagent water: } S_T = 0.09x + 0.004$$
$$S_o = 0.02x - 0.009$$

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Selected water matrices: $S_T = 0.08x + 0.005$

$S_o = 0.02x + 0.004$

3) Titrimetric—Based on the results of six operators in three laboratories, the overall and single-operator precision of this test method within its designated range may be expressed as follows:

Reagent water: $S_T = 0.532 - 0.10x$

$S_o = 0.151 - 0.01x$

Selected water matrices: $S_T = 0.604 - 0.06x$

$S_o = 0.092 + 0.02x$

where:

S_T = overall precision,
S_o = single-operator precision, and
x = cyanide concentration, mg/L.

b. Bias: Recoveries of known amounts of cyanide from reagent water and selected water matrices are shown below.

Medium	Technique	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
Reagent water	Colorimetric	0.030	0.030	25	0.0089	0.000	0
		0.100	0.117	27	0.0251	0.017	17
		0.400	0.361	27	0.0400	–0.039	–10
	Electrode	0.030	0.030	21	0.0059	0.000	0
		0.100	0.095	21	0.0163	–0.005	–5
		0.400	0.365	21	0.0316	–0.035	–9
		1.000	0.940	21	0.0903	–0.060	–6
	Titrimetric	1.00	1.35	18	0.4348	0.35	35
		1.00	1.38	18	0.3688	0.38	38
		4.00	3.67	18	0.1830	–0.33	–8
Selected water matrices	Colorimetric	0.030	0.029	15	0.0062	0.001	3
		0.100	0.118	24	0.0312	0.018	18
		0.400	0.381	23	0.0389	–0.019	–5
	Electrode	0.030	0.029	20	0.0048	–0.001	–3
		0.100	0.104	21	0.0125	0.004	4

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Medium	Technique	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
		0.400	0.357	21	0.0372	–0.043	–11
		1.000	0.935	21	0.0739	–0.065	–7
	Titrimetric	1.00	1.55	18	0.5466	0.55	55
		1.00	1.53	18	0.4625	0.53	53
		4.00	3.90	18	0.3513	–0.10	–3

7. Reference

1. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1987. Research Rep. D2036:19-1131. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- J. Cyanogen Chloride

1. General Discussion

Cyanogen chloride (CNCl) is the first reaction product when cyanide compounds are chlorinated. It is a volatile gas, only slightly soluble in water, but highly toxic even in low concentrations. (CAUTION: *Avoid inhalation or contact*.) A mixed pyridine-barbituric acid reagent produces a red-blue color with CNCl.

Because CNCl hydrolyzes to cyanate (CNO^-) at a pH of 12 or more, collect a separate sample for CNCl analysis (See Section 4500-CN^-.B.2) in a closed container without sodium hydroxide (NaOH). A quick test with a spot plate or comparator as soon as the sample is collected may be the only procedure for avoiding hydrolysis of CNCl due to time lapse between sampling and analysis.

If starch-iodide (KI) test paper indicates presence of chlorine or other oxidizing agents, add sodium thiosulfate ($Na_2S_2O_3$) immediately as directed in Section 4500-CN^-.B.2.

2. Apparatus

See Section 4500-CN^-.E.2.

3. Reagents

a. Reagents listed in Section 4500-CN^-.E.3 and Section 4500-CN^-.H.4.

b. Phosphate buffer: Dissolve 138 g sodium dihydrogen phosphate monohydrate, $NaH_2PO_4 \cdot H_2O$, in water and dilute to 1 L. Refrigerate.

4. Procedure

a. Preparation of standard curve: Pipet a series of standards containing 1 to 10 µg CN^- into 50-mL volumetric flasks (0.02 to 0.2 µg CN^-/mL). Dilute to 20 mL with NaOH dilution

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solution. Use 20 mL of NaOH dilution solution for the blank. Add 2 mL chloramine-T solution and 4 mL phosphate buffer; stopper and mix by inversion two or three times. Add 5 mL pyridine-barbituric acid reagent, dilute to volume with water, mix thoroughly, and let stand exactly 8 min for color development. Measure absorbance at 578 nm in a 10-mm cell using distilled water as a reference. Calculate slope and intercept of the curve.

b. If sample pH is above 8, reduce it to 8.0 to 8.5 by careful addition of phosphate buffer. Measure 20 mL sample portion into 50-mL volumetric flask. If more than 0.20 mg CNCl-CN^-/L is present use a smaller portion diluted to 20 mL with water. Add 1 mL phosphate buffer, stopper and mix by inversion *one* time. Let stand 2 min. Add 5 mL pyridine-barbituric acid reagent, stopper and mix by inversion *one* time. Let color develop 3 min, dilute to volume with water, mix thoroughly, and let stand an additional 5 min. Measure absorbance at 578 nm in 10-mm cell using distilled water as a reference.

5. Calculation

Compute slope (m) and intercept (b) of standard curve as directed in 4500-CN^-.E.5.

$$\text{Cyanogen chloride as } CN^-, \text{ mg/L} = (ma_1 + b) \times \frac{50}{\text{mL sample}}$$

where:

a_1 = absorbance of sample solution.

6. Precision[1]

Cyanogen chloride is unstable and round-robin testing is not possible. Single-operator precision is as follows:

Six operators made 70 duplicate analyses on samples of different concentrations within the applicable range of the method. The overall single-operator precision within its designated range may be expressed as follows:

$$\log S_o = (0.5308 \log c) - 1.9842$$
$$\log R = (0.5292 \log c) - 1.8436$$

where:

c = mg CNCl-CN^-/L,

S_o = single-operator precision in the range of the method (precision is dependent on concentration), and

R = range between duplicate determinations.

The collaborative test data were obtained on reagent-grade water. For other matrices, these data may not apply.

7. Reference

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1. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1989. Research Rep. D4165:19-1100. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- K. Spot Test for Sample Screening

1. General Discussion

The spot test procedure permits quick screening to establish whether more than 50 µg/L of cyanide amenable to chlorination is present. The test also establishes the presence or absence of cyanogen chloride (CNCl). With practice and dilution, the test reveals the approximate concentration range of these compounds by the color development compared with that of similarly treated standards.

When chloramine-T is added to cyanides amenable to chlorination, CNCl is formed. CNCl forms a red-blue color with the mixed reagent pyridine-barbituric acid. When testing for CNCl omit the chloramine-T addition. (CAUTION: *CNCl is a toxic gas; avoid inhalation.*)

The presence of formaldehyde in excess of 0.5 mg/L interferes with the test. A spot test for the presence of aldehydes and a method for removal of this interference are given in Section 4500-CN^-.B.3.

Thiocyanate (SCN^-) reacts with chloramine-T, thereby creating a positive interference. The CN^- can be masked with formaldehyde and the sample retested. This makes the spot test specific for SCN^-. In this manner it is possible to determine whether the spot discoloration is due to the presence of CN^-, SCN^-, or both.

2. Apparatus

a. Porcelain spot plate with 6 to 12 cavities.

b. Dropping pipets.

c. Glass stirring rods.

3. Reagents

a. Chloramine-T solution: See Section 4500-CN^-.E.3*a*.

b. Stock cyanide solution: See Section 4500-CN^-.E.3*b*.

c. Pyridine-barbituric acid reagent: See Section 4500-CN^-.E.3*d*.

d. Hydrochloric acid, HCl, 1 + 9.

e. Phenolphthalein indicator aqueous solution.

f. Sodium carbonate, Na_2CO_3, anhydrous.

g. Formaldehyde, 37%, pharmaceutical grade.

4. Procedure

If the solution to be tested has a pH greater than 10, neutralize a 20- to 25-mL portion. Add about 250 mg Na_2CO_3 and swirl to dissolve. Add 1 drop phenolphthalein indicator. Add

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1 + 9 HCl dropwise with constant swirling until the solution becomes colorless. Place 3 drops sample and 3 drops distilled water (for blanks) in separate cavities of the spot plate. To each cavity, add 1 drop chloramine-T solution and mix with a clean stirring rod. Add 1 drop pyridine-barbituric acid solution to each cavity and again mix. After 1 min, the sample spot will turn pink to red if 50 µg/L or more of CN^- are present. The blank spot will be faint yellow because of the color of the reagents. Until familiarity with the spot test is gained, use, in place of the water blank, a standard solution containing 50 µg CN^-/ L for color comparison. This standard can be made by diluting the stock cyanide solution (¶ 3*b*).

If SCN^- is suspected, test a second sample pretreated as follows: Heat a 20- to 25-mL sample in a water bath at 50°C; add 0.1 mL formaldehyde and hold for 10 min. This treatment will mask up to 5 mg CN^-/L, if present. Repeat spot testing procedure. Color development indicates presence of SCN^-. Comparing color intensity in the two spot tests is useful in judging relative concentration of CN^- and SCN^-. If deep coloration is produced, serial dilution of sample and additional testing may allow closer approximation of the concentrations.

4500-CN^- L. Cyanates

1. General Discussion

Cyanate (CNO^-) may be of interest in analysis of industrial waste samples because the alkaline chlorination process used for the oxidation of cyanide yields cyanate in the second reaction.

Cyanate is unstable at neutral or low pH; therefore, stabilize the sample as soon as collected by adding sodium hydroxide (NaOH) to pH >12. Remove residual chlorine by adding sodium thiosulfate ($Na_2S_2O_3$) (see Section 4500-CN^-.B.2).

a. Principle: Cyanate hydrolyzes to ammonia when heated at low pH.

$$2NaCNO + H_2SO_4 + 4H_2O \rightarrow (NH_4)_2SO_4 + 2NaHCO_3$$

The ammonia concentration must be determined on one sample portion before acidification. The ammonia content before and after hydrolysis of cyanate may be measured by phenate (Section 4500-NH_3.F), or ammonia-selective electrode (Section 4500-NH_3.D) method.[1] The test is applicable to cyanate compounds in natural waters and industrial waste.

b. Interferences:

1) Organic nitrogenous compounds may hydrolyze to ammonia (NH_3) upon acidification. To minimize this interference, control acidification and heating closely.

2) Reduce oxidants that oxidize cyanate to carbon dioxide and nitrogen with $Na_2S_2O_3$ (see Section 4500-CN^-.G).

3) Industrial waste containing organic material may contain unknown interferences.

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c. Detection limit: 1 to 2 mg CNO^-/L.

2. Apparatus

a. Expanded-scale pH meter or selective-ion meter.

*b. Ammonia-selective electrode.**#(3)

c. Magnetic mixer, with TFE-coated stirring bar.

d. Heat barrier: Use a 3-mm-thick insulator under beaker to insulate against heat produced by stirrer motor.

3. Reagents

a. Stock ammonium chloride solution: Dissolve 3.819 g anhydrous NH_4Cl, dried at 100°C, in water, and dilute to 1 L; 1.00 mL=1.00 mg N=1.22 mg NH_3.

b. Standard ammonium chloride solution: From the stock NH_4Cl solution prepare standard solutions containing 1.0, 10.0, and 100.0 mg NH_3-N/L by diluting with ammonia-free water.

c. Sodium hydroxide, 10*N*: Dissolve 400 g NaOH in water and dilute to 1 L.

d. Sulfuric acid solution, H_2SO_4, 1 + 1.

e. Ammonium chloride solution: Dissolve 5.4 g NH_4Cl in distilled water and dilute to 1 L. (Use only for soaking electrodes.)

4. Procedure

a. Calibration: Daily, calibrate the ammonia electrode as in Section 4500-NH_3.F.4*b* and *c* using standard NH_4Cl solutions.

b. Treatment of sample: Dilute sample, if necessary, so that the CNO^- concentration is 1 to 200 mg/L or NH_3-N is 0.5 to 100 mg/L. Take or prepare at least 200 mL. From this 200 mL, take a 100-mL portion and, following the calibration procedure, establish the potential (millivolts) developed from the sample. Check electrode reading with prepared standards and adjust instrument calibration setting daily. Record NH_3-N content of untreated sample (*B*).

Acidify 100 mL of prepared sample by adding 0.5 mL 1 + 1 H_2SO_4 to a pH of 2.0 to 2.5. Heat sample to 90 to 95°C and maintain temperature for 30 min. Cool to room temperature and restore to original volume by adding ammonia-free water. Pour into a 150-mL beaker, immerse electrode, start magnetic stirrer, then add 1 mL 10*N* NaOH solution. With pH paper check that pH is greater than 11. If necessary, add more NaOH until pH 11 is reached.

After equilibrium has been reached (30 s) record the potential reading. Estimate NH_3-N content from calibration curve.

5. Calculations

$$\text{mg } NH_3\text{-N derived from } CNO^-/L = A - B$$

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where:

A = mg NH_3-N/L found in the acidified and heated sample portion and
B = mg NH_3-N/L found in untreated portion.

$$\text{mg } CNO^-/L = 3.0 \times (A - B)$$

6. Precision

No data on precision of this method are available. See Section 4500-NH_3.A.4 for precision of ammonia-selective electrode method.

7. Reference

1. THOMAS, R.F. & R.L. BOOTH. 1973. Selective electrode determination of ammonia in water and wastes. *Environ. Sci. Technol.* 7:523.

4500-CN^- M. Thiocyanate

1. General Discussion

When wastewater containing thiocyanate (SCN^-) is chlorinated, highly toxic cyanogen chloride (CNCl) is formed. At an acidic pH, ferric ion (Fe^{3+}) and SCN^- form an intense red color suitable for colorimetric determination.

a. Interference:

1) Hexavalent chromium (Cr^{6+}) interferes and is removed by adding ferrous sulfate ($FeSO_4$) after adjusting to pH 1 to 2 with nitric acid (HNO_3). Raising the pH to 9 with 1*N* sodium hydroxide (NaOH) precipitates Fe^{3+} and Cr^{3+}, which are then filtered out.

2) Reducing agents that reduce Fe^{3+} to Fe^{2+}, thus preventing formation of ferric thiocyanate complex, are destroyed by adding a few drops of hydrogen peroxide (H_2O_2). Avoid excess H_2O_2 to prevent reaction with SCN^-.

3) Industrial wastes may be highly colored or contain various interfering organic compounds. To eliminate these interferences,[1] use the pretreatment procedure given in ¶ 4*c* below. It is the analyst's responsibility to validate the method's applicability without pretreatment (¶ 4*b*). If in doubt, pretreat sample before proceeding with analysis (¶ 4*c*).

4) If sample contains cyanide amenable to chlorination and would be preserved for the cyanide determination at a high pH, sulfide could interfere by converting cyanide to SCN^-. To preserve SCN^- and CN^-, precipitate the sulfide by adding lead salts according to Section 4500-CN^-.B.2 before adding alkali; filter to remove precipitate.

5) Thiocyanate is biodegradable. Preserve samples at pH <2 by adding mineral acid and refrigerate.

6) If interferences from industrial wastes are not removed as directed in ¶ 4*c* below,

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consider adopting a solvent extraction technique with colorimetric or atomic absorption analysis of the extract.[2,3]

b. Application: 0.1 to 2.0 mg SCN^-/L in natural or wastewaters. For higher concentrations, use a portion of diluted sample.

2. Apparatus

a. Spectrophotometer or filter photometer, for use at 460 nm, providing a light path of 5 cm.

b. Glass adsorption column: Use a 50-mL buret with a glass-wool plug, and pack with macroreticular resin (¶ 3) approximately 40 cm high. For convenience, apply a powder funnel of the same diameter as the buret to the top with a short piece of plastic tubing.

3. Reagents

a. Ferric nitrate solution: Dissolve 404 g $Fe(NO_3)_3 \cdot 9H_2O$ in about 800 mL distilled water. Add 80 mL conc HNO_3 and dilute to 1 L.

b. Nitric acid solution, 0.1*N*: Mix 6.4 mL conc HNO_3 in about 800 mL distilled water and dilute to 1 L.

c. Stock thiocyanate solution: Dissolve 1.673 g potassium thiocyanate (KSCN) in distilled water and dilute to 1000 mL; 1.00 mL 1.00 mg SCN^-.

d. Standard thiocyanate solution: Dilute 10 mL stock solution to 1 L with distilled water; 1.00 mL = 0.01 mg SCN^-.

e. Sodium hydroxide solution, 4 g/L: Dissolve 4 g NaOH in about 800 mL distilled water and dilute to 1 L.

f. Macroreticular resin, 18 to 50 mesh:*#(4) The available resin may not be purified. Some samples have shown contamination with waxes and oil, giving poor permeability and adsorption. Purify as follows:

Place sufficient resin to fill the column or columns in a beaker and add 5 times the resin volume of acetone. Stir gently for 1 h. Pour off fines and acetone from settled resin and add 5 times the resin volume of hexane. Stir for 1 h. Pour off fines and hexane and add 5 times the resin volume of methanol. Stir for 15 min. Pour off methanol and add 3 times the resin volume of 0.1*N* NaOH. Stir for 15 min. Pour off NaOH solution and add 3 times the resin volume of 0.1*N* HNO_3 . Stir for 15 min. Pour off HNO_3 solution and add 3 times the resin volume of distilled water. Stir for 15 min. Drain excess water and use purified resin to fill the column. Store excess purified resin after covering it with distilled water. Keep in a closed jar.

g. Methyl alcohol.

4. Procedure

a. Preparation of calibration curve: Prepare a series of standards containing from 0.02 mg to 0.40 mg SCN^- by pipetting measured volumes of standard KSCN solution into 200-mL volumetric flasks and diluting with water. Mix well. Develop color according to ¶ b

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below. Plot absorbance against SCN^- concentration expressed as mg/50 mL sample. The absorbance plot should be linear.

b. Color development: Use a filtered sample or portion from a diluted solution so that the concentration of SCN^- is between 0.1 and 2 mg/L. Adjust pH to 2 with conc HNO_3 added dropwise. Pipet 50-mL portion to a beaker, add 2.5 mL ferric nitrate, and mix.

Fill a 5-cm absorption cell and measure absorbance against a reagent blank at 460 nm or close to the maximum absorbance found with the instrument being used. Measure absorbance of the developed color against a reagent blank within 5 min from adding the reagent. (The color develops within 30 s and fades on standing in light.)

c. Sample pretreatment:

1) Color and various organic compounds interfere with absorbance measurement. At pH 2, macroreticular resin removes these interfering materials by adsorption without affecting thiocyanate.

2) To prepare the adsorption column, fill it with resin, rinse with 100 mL methanol, and follow by rinses with 100 mL 0.1*N* NaOH, 100 mL 0.1*N* HNO_3, and finally with 100 mL distilled water. If previously purified resin is used, omit these preparatory steps.

3) When washing, regenerating, or passing a sample through the column, as solution level approaches resin bed, add and drain five separate 5-mL volumes of solution or water (depending on which is used in next step) to approximate bed height. After last 5-mL volume, fill column with remaining liquid. This procedure prevents undue mixing of solutions and helps void the column of the previous solution.

4) Acidify 150 mL sample (or a dilution) to pH 2 by adding conc HNO_3 dropwise while stirring. Pass it through the column at a flow rate not to exceed 20 mL/min. If the resin becomes packed and the flow rate falls to 4 to 5 mL/min, use gentle pressure through a manually operated hand pump or squeeze bulb on the column. In this case, use a separator funnel for the liquid reservoir instead of the powder funnel. Alternatively use a vacuum bottle as a receiver and apply gentle vacuum. Do not let liquid level drop below the adsorbent in the column.

5) When passing a sample through the column, measure 90 mL of sample in a graduated cylinder, and from this use the five 5-mL additions as directed in ¶ 3), then pour the remainder of the 90 mL into the column. Add rest of sample and collect 60 mL eluate to be tested after the first 60 mL has passed through the column.

6) Prepare a new calibration curve using standards prepared according to ¶ 4*a*, but acidify standards according to ¶ 4*b*, and pass them through the adsorption column. Develop color and measure absorbance according to ¶ 4*b* against a reagent blank prepared by passing acidified, distilled water through the adsorption column.

7) Pipet 50 mL from the collected eluate to a beaker, add 2.5 mL ferric nitrate solution, and mix. Measure absorbance according to ¶ 4*b* against a reagent blank [see ¶ 6) above].

8) From the measured absorbance value, determine thiocyanate content of the sample or dilution using the absorbance plot.

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9) Each day the column is in use, test a mid-range standard to check absorption curve.

10) Regenerate column between samples by rinsing with 100 mL 0.1*N* NaOH; 50 mL 0.1*N* HNO_3; and 100 mL water. Insure that the water has rinsed empty glass section of the buret. Occasionally rinse with 100 mL methanol for complete regeneration. Adsorbed weak organic acids and thiocyanate residuals from earlier tests are eluted by the NaOH rinse. Leave the column covered with the last rinse water for storage.

5. Calculation

Compute slope (m) and intercept (b) of standard curve as directed in Section 4500-CN^-.E.5.

Calculate thiocyanate concentration as follows:

$$\text{mg } SCN^-/L = (ma_1 + b) \times \text{dilution factor}$$

where:

a_1 = absorbance of sample solution.

6. Precision and Bias[4]

a. Precision: Based on the results of twelve operators in nine laboratories, at four levels of concentration, the precision of the test method within its designated range is linear with concentration and may be expressed as follows:

$$\text{Reagent water: } S_T = 0.093x + 0.0426$$
$$S_o = 0.045x + 0.010$$

$$\text{Water matrix: } S_T = 0.055x + 0.0679$$
$$S_o = 0.024x + 0.182$$

where:

S_T = overall precision, mg/L,

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

x = thiocyanate concentration, mg/L.

b. Bias: Recoveries of known amounts of thiocyanate from reagent water and selected water matrices including natural waters, laboratory effluent, steel mill effluent, and dechlorinated and treated sanitary effluents were as follows:

Medium	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
Reagent	1.42	1.411	30	0.181	–0.009	–0.6

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Medium	Added *mg/L*	Recovered *mg/L*	*n*	S_T	Bias	% Bias
water	0.71	0.683	27	0.091	–0.027	–4
	0.35	0.329	30	0.084	–0.021	–6
	0.07	0.068	30	0.052	–0.002	–3
Selected	1.42	1.408	26	0.151	–0.012	–0.8
water	0.71	0.668	29	0.096	–0.042	–6
matrices	0.35	0.320	29	0.085	–0.030	–9
	0.07	0.050	29	0.079	–0.020	–29

For other matrices these data may not apply.

7. References

1. SPENCER, R.R., J. LEENHEER & V.C. MARTI. 1980. Automated colorimetric determination of thiocyanate, thiosulfate and tetrathionate in water. 94th Annu. Meeting. Assoc. Official Agricultural Chemists, Washington, D.C. 1981.
2. DANCHICK, R.S. & D.F. BOLTZ. 1968. Indirect spectrophotometric and atomic absorption spectrometric methods in determination of thiocyanate. *Anal. Chem.* 43:2215.
3. LUTHY, R.G. 1978. Manual of Methods: Preservation and Analysis of Coal Gasification Wastewaters. FE-2496-16, U.S. Dep. Energy, National Technical Information Serv., Springfield, Va.
4. AMERICAN SOCIETY FOR TESTING & MATERIALS. 1989. Research Rep. D4193:19-1099. American Soc. Testing & Materials, Philadelphia, Pa.

4500-CN^- N. Total Cyanide after Distillation, by Flow Injection Analysis (PROPOSED)

1. General Discussion

a. Principle: Total cyanides are digested and steam-distilled from the sample as in Section 4500-CN^-.C, cyanides amenable to chlorination are digested and steam-distilled from the sample as in Section 4500-CN^-.G, or weak acid dissociable cyanides are digested and steam-distilled from the sample as in Section 4500-CN^-.I, by using the apparatus described in Section 4500-CN^-.C or an equivalent distillation apparatus. In any case, the distillate should consist of cyanide in 0.25*M* NaOH. The cyanide in this distillate is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The absorbance of this red dye is measured at 570 nm and is proportional to the total or weak acid dissociable cyanide in the sample.

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Also see Section 4500-CN^-.A and Section 4500-CN^-.E, and Section 4130, Flow Injection Analysis (FIA).

b . Interferences: Remove large or fibrous particulates by filtering sample through glass wool. Guard against contamination from reagents, water, glassware, and the sample preservation process.

Nonvolatile interferences are eliminated or minimized by the distillation procedure. Some of the known interferences are aldehydes, nitrate-nitrite, and oxidizing agents such as chlorine, thiocyanate, thiosulfate, and sulfide. Multiple interferences may require the analysis of a series of laboratory fortified sample matrices (LFM) to verify the suitability of the chosen treatment. See Section 4500-CN^-.B for a discussion of preliminary treatment of samples to be distilled.

2. Apparatus

Flow injection analysis equipment consisting of:

a. FIA injection valve with sample loop or equivalent.

b. Multichannel proportioning pump.

c. FIA manifold (Figure 4500-CN^-:2) with tubing heater and flow cell. Relative flow rates only are shown. Tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE.*#(5)

d. Absorbance detector, 570 nm, 10-nm bandpass.

e. Injection valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and all reagents with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

a. Carrier solution, 0.25*M*: In a 1-L plastic container dissolve 10.0 g NaOH in 1.00 L water.

b. Phosphate buffer, 0.71*M*: To a 1-L tared container add 97.0 g potassium phosphate, monobasic, anhydrous, KH_2PO_4, and 975 g water. Stir or shake until dissolved. Prepare fresh monthly.

c. Chloramine-T: Dissolve 2.0 g chloramine-T hydrate (mol wt 227.65) in 500 mL water. Prepare fresh daily.

d. Pyridine/barbituric acid: In fume hood, place 15.0 g barbituric acid in a tared 1-L container and add 100 g water, rinsing down sides of beaker to wet the barbituric acid. Add 73 g pyridine (C_5H_5N) with stirring and mix until barbituric acid dissolves. Add 18 g conc HCl, then an additional 825 g water, and mix. Prepare fresh weekly.

e. Stock cyanide standard, 100 mg CN^-/L: In a 1-L container, dissolve 2.0 g potassium hydroxide (KOH) in approximately 800 mL water. Add 0.250 g potassium cyanide (KCN).
CAUTION: *KCN is highly toxic. Avoid inhalation of dust or contact with the solid or solutions.*

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Make to final weight of 1000 g with water and mix. Prepare fresh weekly or standardize weekly using procedure in Section 4500-CN^-.D.4.

f. Standard cyanide solution: Prepare cyanide standards in the desired concentration range, using the stock cyanide standard (¶ 3*e*) and diluting with the 0.25*M* NaOH carrier (¶ 3*a*).

4. Procedure

Set up a manifold equivalent to that in Figure 4500-CN^-:2 and follow method supplied by manufacturer or laboratory standard operating procedure for this method. Follow quality control guidelines outlined in Section 4020.

5. Calculation

Prepare standard curves by plotting absorbance of standards processed through manifold versus cyanide concentration. The calibration curve is linear.

6. Precision and Bias

a. Recovery and relative standard deviation: The results of single-laboratory studies with various matrices are given in Table 4500-CN^-:I.

b. MDL without distillation: Using a published MDL method,[1] analysts ran 21 replicates of an undistilled 0.010-mg CN^-/L standard with a 780-µL sample loop. These gave a mean of 0.010 mg CN^-/L, a standard deviation of 0.00012 mg CN^-/L, and an MDL of 0.0003 mg CN^-/L. A lower MDL may be obtained by increasing the sample loop volume and increasing the ratio of carrier flow rate to reagent flow rate.

c. MDL with distillation: Using a published MDL method,[1] analysts ran 21 replicates of a 0.0050-mg CN^-/L standard distilled using the distillation device†#(6) equivalent to the apparatus specified in 4500-CN^-.C. When the 0.25*M* NaOH distillates were determined with a 780-µL sample loop, they gave a mean of 0.0045 mg CN^-/L, a standard deviation of 0.0002 mg CN^-/L, and an MDL of 0.0006 mg CN^-/L.

d. Precision study: Ten injections of an undistilled 0.050-mg CN^-/L standard gave a relative standard deviation of 0.21%.

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1989. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 rev. 12.11 amended June 30, 1986. 49 CFR 43430.

4500-CN^- O. Total Cyanide and Weak Acid Dissociable Cyanide by Flow Injection Analysis (PROPOSED)

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1. General Discussion

a. Principle: Total cyanide consists of various metal-cyanide complexes. To break down or digest these complexes to yield HCN, the sample is mixed with heated phosphoric acid and then irradiated with ultraviolet radiation. The resulting ‘‘donor stream’’ contains the product HCN (aq). This donor stream is passed over a silicone rubber gas permeation membrane. The HCN from the donor stream is extracted by the membrane as HCN (g) and is trapped in a parallel ‘‘acceptor stream’’ that consists of dilute sodium hydroxide, the equivalent of the distillate resulting from the digesting distillations in the sample preparation methods Section 4500-CN^-.C, Section 4500-CN^-.G, and Section 4500-CN^-.I.

As in Section 4500-CN^-.N, the cyanide in this acceptor stream or distillate is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at pH less than 8. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The absorbance of this red dye is measured at 570 nm and is proportional to the total or weak acid dissociable cyanide in the sample.

The weak acid dissociable (WAD) cyanide method is similar except that ultraviolet radiation and phosphoric acid are not used in the donor stream. Instead, a solution of dihydrogen phosphate is used as the donor stream.

Also see Section 4500-CN^-.A, Section 4500-CN^-.E, and Section 4500-CN^-.N and Section 4130, Flow Injection Analysis (FIA).

b. Interferences: Remove large or fibrous particulates by filtering the sample through glass wool. Guard against contamination from reagents, water, glassware, and the sample preservation process.

Nonvolatile interferences are eliminated or minimized by the gas-permeable membrane.

Multiple interferences may require the analysis of a series of sample matrices with known additions to verify the suitability of the chosen treatment. See Section 4500-CN^-.B for a discussion of preliminary treatment of samples that will be distilled.

1) Total cyanide interferences—Sulfide up to a concentration of 10 mg/L and thiocyanate up to a concentration of 20 mg/L do not interfere in the determination of 100 μg CN^-/L. When a sample containing nitrate at 100 mg NO_3^--N/L and 20 mg/L thiocyanate was treated with sulfamic acid, the determined value was 138.2 μg CN^-/L for a known concentration of 100 μg CN^-/L. When pretreated with ethylenediamine, a sample containing 50 mg formaldehyde/L did not interfere in the determination of cyanide.

2) WAD interferences—Sulfide up to 10 mg/L and thiocyanate up to 50 mg/L do not interfere in the determination of 0.1 mg/L cyanide.

2. Apparatus

Flow injection analysis equipment consisting of:

a. FIA injection valve with sample loop or equivalent.

b. Multichannel proportioning pump.

c. FIA manifold (Figure 4500-CN^-:3) with tubing heater, in-line ultraviolet digestion

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fluidics, a gas-permeable silicone rubber membrane and its holder, and flow cell. In Figure 4500-CN^-:3, relative flow rates only are shown. The tubing volumes are given as an example only; they may be scaled down proportionally. Use manifold tubing of an inert material such as TFE. The ultraviolet unit should consist of TFE tubing irradiated by a mercury discharge ultraviolet lamp emitting radiation at 254 nm.

d. Absorbance detector, 570 nm, 10-nm bandpass.

e. Injection valve control and data acquisition system.

3. Reagents

Use reagent water (>10 megohm) for all solutions. To prevent bubble formation, degas carrier and all reagents with helium. Pass He at 140 kPa (20 psi) through a helium degassing tube. Bubble He through 1 L of solution for 1 min. As an alternative to preparing reagents by weight/weight, use weight/volume.

a. Phosphoric acid donor stream (total cyanide): To a 1-L volumetric flask, add approximately 700 mL water, then add 30 mL conc phosphoric acid, H_3PO_4. Mix and let solution cool. Dilute to mark. Prepare fresh monthly.

b. Dihydrogen phosphate donor stream (WAD cyanide): To a tared 1-L container add 97 g anhydrous potassium dihydrogen phosphate, KH_2PO_4, and 975 g water. Stir for 2 h or until the potassium phosphate has gone into solution. Degas with helium. Prepare fresh monthly.

c. NaOH acceptor stream, carrier, and diluent (total and WAD cyanide), 0.025*M* NaOH: To a 1-L container add 1.0 g sodium hydroxide (NaOH) and 999 g water. Mix with a magnetic stirrer for about 5 min. Cover with a laboratory film. Degas with helium. Prepare fresh daily.

d. Buffer (total and WAD cyanide), 0.71*M* phosphate: To a 1-L tared container add 97.0 g potassium phosphate, monobasic, anhydrous, KH_2PO_4, and 975 g water. Stir or shake until dissolved. Prepare fresh monthly.

e. Chloramine-T solution (total and WAD cyanide): Dissolve 3 g chloramine-T hydrate in 500 mL water. Degas with helium. Prepare fresh daily. NOTE: Chloramine-T is an air-sensitive solid. Preferably discard this chemical 6 months after opening.

f. Pyridine/barbituric acid solution (total and WAD cyanide): In the fume hood, place 15.0 g barbituric acid in a tared 1-L container and add 100 g water, rinsing down the sides of the beaker to wet the barbituric acid. Add 73 g pyridine (C_5H_5N) with stirring and mix until the barbituric acid dissolves. Add 18 g conc HCl, then add an additional 825 mL water and mix. Prepare fresh weekly.

g. Stock cyanide standard, 100 mg CN^-/L: In a 1-L container dissolve 2.0 g potassium hydroxide, KOH, in approximately 800 mL water. Add 0.250 g potassium cyanide, KCN. CAUTION: *KCN is highly toxic. Avoid inhalation of dust or contact with the solid or solutions.* Make to final weight of 1000 g with water and invert three times to mix. Prepare fresh weekly or standardize weekly using the procedure in Section 4500-CN^-D.4.

h. Standard cyanide solutions: Prepare cyanide standards in the desired concentration

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range, using the stock cyanide standard (¶ 3*g*) and diluting with the NaOH standards diluent (¶ 3*c*).

4. Procedure

Set up a manifold equivalent to that in Figure 4500-CN^-:3 and follow the method supplied by the manufacturer or laboratory standard operating procedure for this method. Follow quality control guidelines outlined in Section 4020.

5. Calculations

Prepare standard curves by plotting absorbance of standards processed through the manifold vs. cyanide concentration. The calibration curve is linear.

6. Precision and Bias

a. MDL, total cyanide: A 420-µL sample loop was used in the total cyanide method. Using a published MDL method[1], analysts ran 21 replicates of a 10.0-µg CN^-/L standard. These gave a mean of 9.69 µg CN^-/L, a standard deviation of 0.86 µg CN^-/ L, and an MDL of 2.7 µg CN^-/L.

b. MDL, WAD cyanide: A 420-µL sample loop was used in the WAD cyanide method. Using a published MDL method[1], analysts ran 21 replicates of a 10.0-µg CN^-/L standard. These gave a mean of 11.5 µg CN^-/L, a standard deviation of 0.73 µg CN^-/ L, and an MDL of 2.3 µg CN^-/L.

c. Precision study, total cyanide: Seven injections of a 100.0-µg CN^-/L standard gave a relative standard deviation (RSD) of 1.0%.

d. Precision study, WAD cyanide: Ten injections of a 200.0-µg CN^-/L standard gave an RSD of 1.3%.

e. Recovery of total cyanide: Two injections each were made of solutions of potassium ferricyanide and potassium ferrocyanide, both at a concentration equivalent to 100 µg CN^-/L. Both gave an average recovery of 98%.

7. Reference

1. U.S. ENVIRONMENTAL PROTECTION AGENCY. 1989. Definition and procedure for the determination of method detection limits. Appendix B to 40 CFR 136 rev. 12.11 amended June 30, 1986. 49 CFR 43430.

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Endnotes

1 (Popup - Footnote)
* APPROVED BY STANDARD METHODS COMMITTEE, 1997.
2 (Popup - Footnote)
* Orion Model 94-06A or equivalent.
3 (Popup - Footnote)
* Orion Model 95-10, EIL Model 8002-2, Beckman Model 39565, or equivalent.
4 (Popup - Footnote)
* Amberlite® XAD-7, or equivalent.
5 (Popup - Footnote)
* Teflon or equivalent.
6 (Popup - Footnote)
† MICRO DIST, Lachat Instruments, Milwaukee, WI.

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