Designation: D 4374 – 9800

Standard Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Ð Acid dissociable Cyanide, and Thiocyanate[1]

This standard is issued under the fixed designation D 4374; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 These test methods cover the determination of different species of cyanides and thiocyanate in water and waste water,

[1] These test methods are under the jurisdiction of ASTM Committee D-19 on Water and are the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

Current edition approved ~~July~~ June 10, ~~1998.~~ 2000. Published ~~December 1998.~~ September 2000. Originally published as D 4374 – 84. Last previous edition D 4374 – 9~~3~~8.

namely acid dissociable cyanide, total cyanide, and thiocyanate **(1)**.[2]

1.1.1 *Total Cyanide*— This test method determines all the acid dissociable cyanides and the strong metal-cyano-complexes, such as ferrocyanide $[Fe(CN)_6]^{4-}$, ferricyanide $[Fe(CN)_6]^{3-}$, hexacyanocolbaltate $[Co(CN)_6]^{3-}$, and those of gold and platinum.

1.1.2 *Acid Dissociable Cyanide*—This test method basically determines free cyanides, as CN^- and HCN, and weak metal-cyano-complexes such as $[Cd(CN)_4]^{2-}$ and $[Mn(CN)_6]^{3-}$. Iron complexes are not included.

1.1.3 Cyanide complexes, strong complexes like those of iron, cobalt, etc., can be determined by difference, that is, cyanide complexes = total cyanides − acid dissociable cyanides.

1.1.4 *Thiocyanate*— This test method determines the thiocyanate as the difference between another measurement that includes total cyanide plus thiocyanate and the value of total cyanide, that is, thiocyanate = total cyanide plus thiocyanate − total cyanide.

1.2 Cyanates and cyanogen halides are not detected. Cyanogen chloride hydrolyzes to cyanate at the pH of sample preservation (≥12).

1.3 Most of the organo-cyano-complexes are not measured, with the exception of the weak cyanohydrins.

1.4 These test methods apply to different types of water, waste water (raw sewage, sludge, and effluent), sludge, some industrial waste, and sediments. Sample matrixes should be evaluated by the user. The reported precision and bias (see Section 16) may not apply to all samples.

1.5 The values stated in SI units are to be regarded as the standard.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[3]
D 1193 Specification for Reagent Water[3]
D 2036 Test Methods for Cyanides in Water[4]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[3]
D 3864 Guide for Continual On-Line Monitoring Systems for Water Analysis[3]
D 4193 Test Method for Thiocyanate in Water[4]
D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[3]
D 5788 Guide for Spiking Organics Into Aqueous Samples[3]
D 5789 Practice for Writing Quality ControL Specifications for Standard Test Methods for Organic Constituents[3]

3. Terminology

3.1 *Definitions*—For definition of terms relating to water, refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *distillation ratio*, % =

$$\frac{\text{volume of distilled portion of sample}}{\text{total volume of acidified sample}} \times 100$$

4. Summary of Test Method

4.1 Some automated continuous flow modules are used (see Guide D 3864) in addition to the newly developed on-line thin film distillation **(2)** and ultraviolet (UV) irradiation **(3)** .

4.2 Three factors control the separation of cyanides from the samples, namely (*a*) UV irradiation, (*b*) pH and acidification, and (*c*) temperature and time of distillation (see 7.4, 7.5, and 7.3).

4.3 Acidification is made to pH < 1, but the sample exposure to heat treatment in the continuous thin film distillation is very short (few seconds). Thus the liberation of HCN is only from the free cyanides and the weak cyanide complexes, that is, the acid dissociable cyanides, and not from the strong complexes. (Acidification to pH 4.5 gives the same acid dissociable cyanide results.)

4.4 For total cyanides the breakdown of the strong metal cyanide complexes, prior to the thin film distillation, is achieved by UV irradiation **(4)**. Quartz is transparent to the full range of UV wavelengths, 200 to 400 nm, and allows for the breakdown of the strong metal cyanide complexes as well as thiocyanate. On the other hand, borosilicate glass filters out a major portion of the UV irradiation and transmits only the wavelengths longer than 300 nm, which with longer irradiation time at alkaline pH can break down all the strong Co and Fe cyanide complexes, but not the thiocyanate **(1)**.

4.5 Absorption of the liberated HCN gas is carried out using a glass coil and 0.02 *M* sodium hydroxide solution (see 7.5).

---

[2] The boldface numbers in parentheses refer to the list of references at the end of the text.
[3] *Annual Book of ASTM Standards*, Vol 11.01.
[4] *Annual Book of ASTM Standards*, Vol 11.02.

4.6 Colorimetric determination of the recovered cyanides is made by pyridine-barbituric acid reagent. The color is developed at pH 5.5 to 6.0 and is measured at 578 nm (or use a 580 nm filter).

4.7 The lower limit of detection for these automated methods is ≤0.5 µg/L (when using a 50 mm flow cell and depending on the working range).

5. Significance and Use

5.1 Cyanides are known to be toxic to man, but more so to fish and other aquatic life. The complexity of the chemistry of cyanides has led to the coexistence of several cyanide species in the environment. The presence of cyanides in industrial, domestic, and surface water is cause for concern. Several regulations and standards require continuous monitoring of cyanides in different types of water and wastes. The automated test methods presented offer useful tools for such monitoring. (See also Practice D 4193.)

6. Interferences and Treatment

6.1 Several interferences are encountered with cyanide analysis (see Test Methods D 2036). The known interferents with the automated system are turbidity and color-contributing substances, sulfides, oxidizing materials, nitrate-nitrite, some metal cations, aldehydes, fatty acids, and some potential cyanide-forming materials. Many of these interferences could be treated, however care should be taken to reduce the time of sample handling and minimize exposure to UV light **(5, 6)**. (Fig. 1 is a flow diagram for cyanide measurements.)

6.2 *Turbidity and Color Contributing Substances*—These may interfere with color measurement. However, most of these substances are removed automatically through the thin film distillation step prior to color development.

6.3 *Sulfides*—Sulfides may cause direct or indirect interferences, or both, with cyanide measurements.

6.3.1 *Direct Sulfide Interference* —Sulfide competes with cyanide in the reaction with the colorimetric reagents. The degree of sulfide interference depends on the concentrations of sulfide, cyanide, and chloramine-T solution. At the specified conditions, the cyanide automated system can tolerate the presence of sulfides up to about 10 mg/L without significant interference.

6.3.2 *Indirect Sulfide Interference* —Sulfide may react with cyanide and form thiocyanate. The reaction kinetics depend on the concentration of sulfide and cyanide ions as well as the pH. Higher pH values accelerate the reaction.

6.3.3 *Treatment for Sulfides*—Sulfide-containing samples should be treated as follows. Treatment by dilution is recommended when samples are to be analyzed rapidly, whereas treatment with lead or cadmium carbonate should be done before storage.

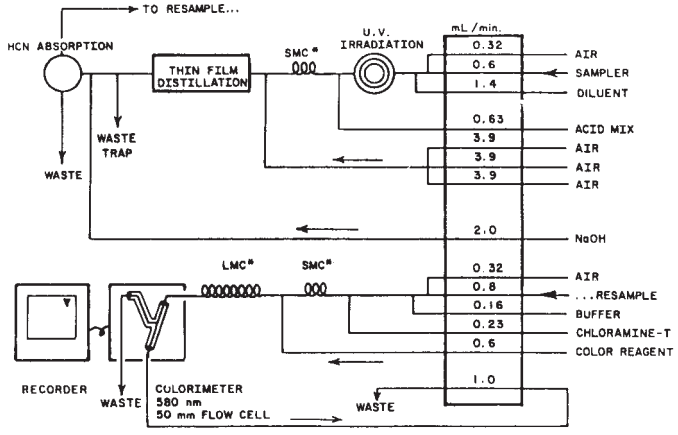
6.3.3.1 *Treatment by Dilution*—Dilute the sample with distilled water (within the detection limits of the test method) until the lead acetate paper test becomes negative (the sensitivity of this test is about 5 mg/L sulfide). Thus the sulfide concentration will be below the interfering level. Proceed with the analysis taking into account the dilution factor.

6.3.3.2 *Treatment with Lead or Cadmium Carbonate*—This treatment is recommended to be made before preservation if possible: Add small amounts of powdered carbonate to the stabilized sample. Repeat addition until no further dark lead sulfide or yellow cadmium sulfide precipitates, and the lead acetate paper test becomes negative. Avoid large excess of carbonate and long contact time to minimize cyanide losses.

6.3.4 For more information refer to Appendix X1[5].

6.4 *Oxidizing Materials*:

[5] Permission has been granted by the Metropolitan Water Reclamation District of Greater Chicago (MWRDGC) to include additional data on interferences.



* SMC and LMC: Short (5 turns) and long (28 turns) mixing coils.
Total Cyanide: Acidification after alkaline UV.
Total Cyanide Plus Thiocyanate: Acidification before UV.
Dissociable Cyanide: Bypass UV irradiation.

FIG. 1 Flow Diagram for Cyanide Measurements

6.4.1 Oxygen, ozone, chlorine, and other oxidants may oxidize the free and some weak complex cyanides to cyanate and results in lower cyanide values. It should be realized that treatment with reducing agents is to prevent further oxidation but cannot recover what has been already oxidized. Several reducing agents, such as ascorbic acid ($C_6H_8O_6$), sodium hydrogen sulfite ($NaHSO_3$), sodium thiosulfate ($Na_2S_2O_3$), stannous chloride ($Sn Cl_2$), and hypophosphorous acid (H_3PO_3), were evaluated and found not satisfactory. They either cause interferences themselves or did not demonstrate efficient reduction. On the other hand, oxalic acid [$(COOH)_2$], sodium arsenite [$(NaAsO_2)$], and sodium borohydride [$NaBH_4$] were found to be effective in many cases.

6.4.2 Oxalic acid, about 2 g/L, can reduce up to 50 mg chlorine per litre. The reaction is satisfactory, though somewhat slow and requires acidic or neutral pH. Therefore, treat with oxalic acid and close the sample container. Wait 15 min, then preserve with sodium hydroxide.

6.4.3 Sodium arsenite was found to be very efficient in reduction. Only 0.1 g/L is required to reduce 50 mg chlorine per litre. The reaction is fast and the arsenite could be added before or after sodium hydroxide. However, in some cases treatment of field samples with arsenite caused interferences and resulted in unexpectedly high cyanide values (refer to 6.5 and Appendix X2). In addition, sodium arsenite is highly toxic and safer alternatives should be used.

6.4.4 Sodium borohydride was ~~also~~ found to be very effective in reduction. Only 0.1 g/L can reduce more than 50 mg chlorine per litre. When used it should be added in alkaline medium to lengthen its reducing action (in acid it will release all its hydrogen rapidly and loses its effectiveness). In addition, sodium borohydride could be used for treatment of aldehyde interference (see 6.6).

6.4.5 Addition of these reducing agents enhances the interference of nitrate-nitrite. Careful considerations should be taken in cases where nitrate-nitrite may be present, especially with alkaline UV irradiation (see 6.5 and Appendix X2).

6.5 *Nitrate-Nitrite Interference* :

6.5.1 There is no interference by nitrate or nitrite with acid dissociable cyanide measurement.

6.5.2 Nitrite interferes significantly with total cyanide measurement. (Nitrate does not interfere unless reduced to nitrite). Nitrite interference is positive under acidic conditions and negative with alkaline pH and UV irradiation.

6.5.3 Nitrite interference is much greater with most field samples than with synthetic water standards. The interference is more pronounced in presence of reducing agents such as sodium hydrogen sulfite, sodium arsenite, or sodium borohydride (see 6.4 and Appendix X2).

6.5.4 Sulfamic acid was found to be effective in removal of nitrite interference. Addition of 2 g sulfamic acid per litre of digestive acid mixture readily removes up to 100 mg/L of nitrite. Treatment with sufamic acid must be before the alkaline UV irradiation (see Fig. 2). With effective high speed UV irradiation and distillation, as described in ~~7.4.4,~~ 7.6, complete cyanide recovery was achieved in presence of 1g/L nitrite and gradually decreases to about 50 % and 20 % at 5 and 10 g/L Nitrite. Treatment with sulfamic acid is more effective when irradiation is all acidic, in which case no interference is observed up to 10 g/L nitrite.

6.5.5 Refer to Appendix X2 for more information.

6.6 *Aldehydes*:

6.6.1 Aldehydes react with cyanide and cause negative interference (probably due to formation of nitriles). This interference is

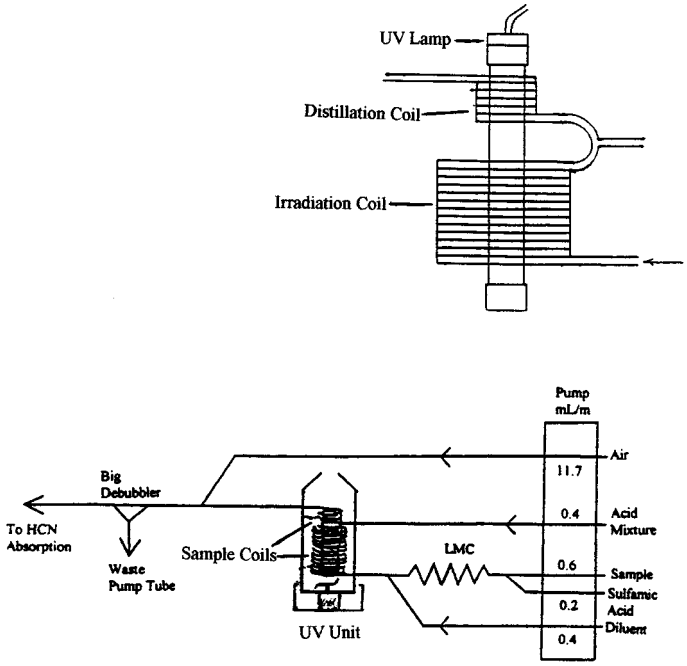


FIG. 2 Partial Manifold for Total Cyanide (Before Color Development)

noticeable at formaldehyde concentrations of 0.5 mg/L and above. Both total cyanide and acid dissociable cyanide are affected by the presence of aldehydes and significant cyanide losses occur.

6.6.2 Treatment with silver nitrate **(7)** gave erratic results, whereas ethylene diamine was found to be reasonably effective.

6.6.3 The addition of 2 mL of 5 % ethylene diamine solution per 100-mL sample gives satisfactory recovery of total cyanides in presence of up to 50 mg/L formaldehyde. Recovery of acid dissociable cyanides is not satisfactory. Variable losses occur depending on the levels of cyanide, aldehyde, and amount of ethylene diamine added.

6.6.4 For more information refer to Appendix X3.

6.6.5 Treatment with sodium borohydride was effective. Satisfactory results were obtained with both total cyanide and acid dissociable cyanide in the presence of 1 g/L formaldehyde. Sodium borohydride should be added in alkaline pH and could be added with the diluent in the automated system (see diluent composition and preparation in 8.8).

NOTE 1—**Caution**—For total cyanide sodium borohydride should not be added before proper treatment of nitrite (see 6.5 and Appendix X2).

6.7 *Unknown Negative Interferences with Total Cyanide Measurement*:

6.7.1 It was noticed that some effluents of sewage treatment plants and some industrial waste samples gave with alkaline UV total cyanide values lower than the acid dissociable cyanide. In addition, cyanide spike recoveries were very poor, which should never be the case.

6.7.2 Changing the UV irradiation conditions from alkaline to acidic eliminates this problem and good cyanide recoveries are obtained. This should not be done in presence of high thiocyanate levels, otherwise about 15 % of thiocyanate will be included in the total cyanide measurement. Furthermore, some losses may be observed due to incomplete breakdown of strong cyanide complexes. About 80 % from cobalt complexes and 5 to 10 % from iron complexes will not be recovered. However, addition of the diluent containing sodium borohydride decreases the thiocyanate interference and improves the cyanide iron complexes recovery.

6.7.3 With the high speed UV irradiation and distillation ~~(7.4.4~~ (7.6 and Fig. 2) and addition of acid mixture before the ~~narrow irradiation~~ upper distillation coil, complete recovery of all strong iron complexes is achieved, as well as better cobalt cyanide complex recovery (about 40 %). Also, thiocyanate is not detected by this short and fast acidic UV exposure.

6.8 *Fatty Acids*:

6.8.1 Mineral oils do not cause any interferences. Fatty acids up to 100 mg/L are tolerated by the cyanide automated system. Higher concentrations of fatty acids interfere mechanically with the automated thin film distillation technique. Apparently the presence of fatty acids leads to the escape of gases through the waste trap system. In addition fatty acids may distill over and form soap with the NaOH absorbing solution and interfere with the cyanide colorimetric determination.

6.8.2 Excessive amounts of fatty acids can be removed by liquid-liquid extraction. Extraction at a pH 6–7 **(8)** may cause significant cyanide losses (up to 50 %). Extraction at pH 12 with trichlorotrifluoroethane, hexane, or isooctane is adequate and cyanide recoveries are satisfactory (about 90 %). Use a solvent volume about ⅕ of the sample. One or two extractions should reduce the fatty acids below the interfering level. Salting-out effect by the addition of NaCl (5 to 9 g per 500-mL sample) enhances the extraction and separation.

6.9 *Metal Cations*:

6.9.1 Metal cations do not interfere with total cyanide measurement, because UV irradiation breaks down all the cyanide complexes. Formation of metal cyanide complexes in field samples is not considered a source of interference to the measurement of acid dissociable cyanide since the objective is not to measure the strong cyanide complexes.

6.9.2 On the other hand, addition of some metallic catalytic compounds during the analytical procedure is not desirable and may introduce significant errors. Dramatic inhibition occurs when mercuric chloride and, to a lesser extent, cuprous chloride were added as catalysts. Magnesium chloride, while not causing any problems, did not demonstrate any favorable catalytic action. Thus no catalysts should be added.

6.9.3 Due to its high volatility, mercury when present at concentrations > 1 mg/L distills over with the cyanide causing negative interference. Most samples do not contain mercury at this high level.

6.10 *Potential Cyanide-Forming Materials* :

6.10.1 Several substances, namely cyanate, nitrobenzene, urea, thiourea, glycine, and cysteine, were investigated to determine if they hydrolyze or break down under the experimental conditions and interfere with the cyanide determination.

6.10.2 None of these materials gave interferences in the acid dissociable cyanide measurement.

6.10.3 Only few sulfur-containing substances gave variable positive interferences with the total cyanide determination. Each 1 mg/L thiourea produces a response of about 5 µg/L CN. Cysteine interferes only at very high levels and can be considered negligible up to 100 mg/L. Thiourea and cysteine are not likely to be found in significant concentrations in natural or waste water.

7. Apparatus

7.1 A one, two, or three channel automated system could be made, using the following modules:

7.1.1 *Sampler*, 20 samples per hour (1:1).

7.1.2 *Proportioning Pump*.

7.1.3 *Colorimeter*, with a 580-nm filter and a 15 or 50 mm flow cell (depending on the desirable range).

7.1.4 *Recorder*.

7.1.5 *Printer or Data System*, (optional).

7.2 *Manifold*, the flow diagram and details of which are presented in Fig. 1 and Fig. 2. Note the thin film distillation unit and the UV irradiator.

7.3 *Ultraviolet (UV) Irradiator* —Fig. ~~2~~ 3 presents a schematic of the UV irradiator used for the breakdown of the complex cyanides and thiocyanate **(3)**. It consists of the following components:

7.3.1 *UV Photo-Chemical Lamp*, 550-W.

7.3.2 *Transformer*, a-c, 550 W, 105 to 125 V, 60 cycles, with an on-off switch and a tickler circuit.

7.3.3 *Cooling Miniature Fan*, 12 by 7.5 cm, 115 V, 60 cycles (activated by the same switch as the UV lamp).

7.3.4 *Borosilicate Glass Coil*, (for total cyanide) made from 2.4 mm inside diameter tubing, the coil is 8 cm in diameter and twelve turns (to give 5 min irradiation time).

7.3.5 *Quartz Coil*, (for total cyanide plus thiocyanate), similar to the borosilicate coil but only five turns (to give two minutes irradiation time).

7.3.6 *Housing of UV Irradiator*.

7.4 *Thin Film Distillation Unit* —~~(2)~~:

7.4.1 The unit is made of borosilicate glass tubing and a schematic is presented in Fig. ~~3~~ 4. It consists of a horizontal tube (*A*), 8-mm inside diameter (10-mm outside diameter), 25 cm long, and is slightly tilted downwards with a slope of about 5°. The tube accommodates the continuous flow of acidified samples. The horizontal tube is connected to a vertical tube (*B*), 5-mm inside diameter and 170 mm long, to carry the HCN gas evolved to the absorber. The nondistilled portion of the acidified sample flows to the waste trap (*C*).

7.4.2 *Waste Trap*—The waste trap is a two-piece unit. The inside piece connects to the distillation unit by a 12/5 spherical joint and clamp (S/P No. C6120-1, Size 12). This inner piece is placed into the outer jacketing tube (200 by 22-mm) by means of a 19/22 ground glass joint. When in operation, the nondistilled waste flows by gravity from the distillation unit to the waste outlet.

7.4.3 *Heating and Temperature Control* —The unit basically consists of an aluminum bar and temperature control components. The aluminum bar (see Fig. ~~4)~~ 4) dissipates heat to the thin film of the acidified sample. The temperature of the heating bar is regulated with a 150-W cartridge heater and a variable transformer. The temperature is monitored by a dial thermometer.

~~7.4.4 *Aluminum Bar and Heating Cartridge* , can be replaced by using a small glass coil, 30 mm in diameter and 5 turns, around and close to the (hot) UV lamp. The temperature could be optimized by the fan speed control. For dissociable cyanide the UV irradiation should be blocked by using or painted opaque upper small heating coil, and bypass the lower irradiation coil. In this case, both the horizontal and vertical tubes of the thin film distillation unit could be much shorter, 30 mm, or simpler, replaced by a big debubbler and a waste pump tube. Also, by using narrow coils (1–2 mm I.D.) the UV irradiation and heating are more effective and the analytical flow is suitable for both continuous flow injection and segmented flow systems.~~

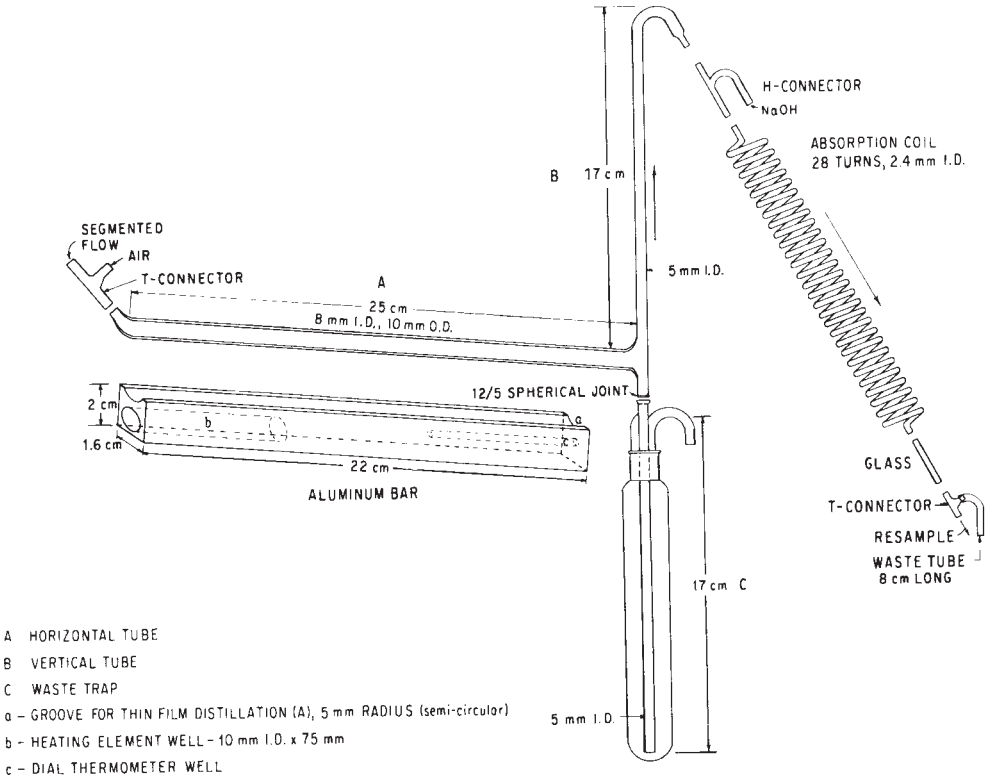


FIG. 3 Continuous Thin Film Distillation Unit

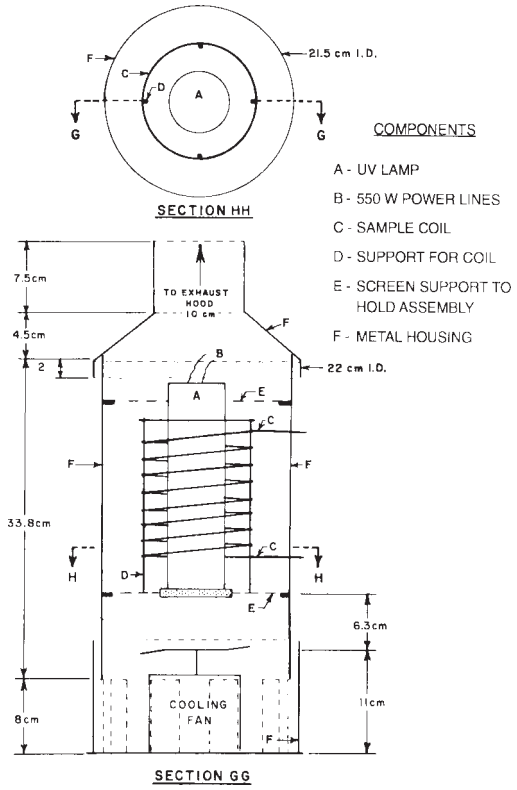


FIG. 4 Ultraviolet Irradiation Unit (Lamp, Coil, and Housing)

7.5 *Gas Absorber*— Absorption of HCN gas is achieved by forcing the gas mixture and 0.02 *M* NaOH solution through an absorption glass ~~coil (2.4-mm inside diameter and 28 turns),~~ coil, as shown in Fig. 4. The coil should be sloped downwards to ease the flow.

7.6 *Ultraviolet Irradiation-Distillation Unit*[6]—This unit replaces both UV irradiator (7.3) and thin film distillation unit (7.4). See Fig. 2 with the enlarged view of the sample coils, namely the irradiation coil (12 turns, 45 mm diameter) and the upper distillation coil (5 turns, 30 mm diameter). The small glass distillation coil replaces the complicated thin film distillation and waste system, and is placed around and close to the hot UV lamp. The temperature for optimum distillation is controlled by the fan speed. The HCN gas is separated by a big debubbler and directed to the absorption coil.

7.6.1 For acid dissociable cyanide, the distillation unit should be opaque or painted to block any UV irradiation and bypass the lower irradiation coil.

7.7 Also, by using narrow coils (1–2 mm tubing I.D.) the UV irradiation and distillation are more effective and the analytical flow is suitable for both continuous flow injection and segmented flow systems.

7.8 *Some Important Connections* :

7.~~6~~8.1 The air flow (from the three pump tubes) and the segmented flow from the UV irradiator should lead directly (simultaneously) into the thin film distillation unit by means of a glass connector with fluorocarbon sleeve. Do not use any flexible tubing between the glass connector and the distillation unit.

7.~~6~~8.2 Do not use flexible tubing between the thin film distillation and the absorption coil, nor from the absorption coil to the debubbler before resampling. These connections should be made with glass tubing and fluorocarbon sleeves.

7.~~6~~8.3 The waste tube from the debubbler, before resampling, should be wide and as short as possible (<8 cm) with a free ending.

8. Reagents

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all

~~*Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.~~

[6] US Patent 5,965,450–by Kelada, 1999.

reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, [7] where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*— Unless otherwise indicated, references to water (not sample water) shall be understood to mean reagent water conforming to Specification D 1193, Type II.

8.3 *Reagents for Screening and Treatment of Interferences*:

8.3.1 *Lead Acetate and Potassium Iodide-Starch Paper*.

8.3.2 *Lead or Cadmium Carbonate* .

8.3.3 *Oxalic Acid and Sodium Arsenite* .

8.3.4 *Ethylene Diamine*.

8.3.5 *Trichlorotrifluoroethane, Hexane, or Isooctane*.

8.4 *Sodium Hydroxide (NaOH),* for preservation and other preparations:

8.4.1 *Stock Solution,* 40 g/L (1.0 *M*)—Dissolve 40 g of NaOH in distilled water and dilute to 1 L.

8.4.2 *Working Solution,* 0.8 g/L (0.02 *M*)—Dilute 100 mL of the stock solution (see 8.4.1) to 5 L. This solution is used in the following: (*a*) absorption of HCN gas, (*b*) preparation of cyanide standards and (*c*) routine cleaning of the system manifold.

8.5 *Reagents for Standardization* :

8.5.1 *Silver Nitrate Solution,* 0.0192 *N Standard* (1 mL = 1 mg CN)—Weigh 3.27 g of $AgNO_3$ crystals (oven dried), dissolve in water and dilute to 1 L. Keep in a dark container. Standardize against standard sodium chloride (NaCl) solution using the argentometric method **(7)** with potassium chromate (K_2CrO_4) indicator. One millilitre of this solution = 1 mg CN.

8.5.2 *Rhodamine Indicator*—Dissolve 20 mg of 5-(*p*-dimethylaminobenzylidene)rhodanine in 100 mL acetone.

8.6 *Cyanide and Thiocyanate Standards* :

8.6.1 *Simple Cyanide Solution, Stock* (1.0 g/L CN)—In a 100 mL flask dissolve 0.251 g of potassium cyanide (KCN) in about 80 mL water. Add about five pellets of sodium hydroxide, shake well to dissolve. Then dilute to the mark.

8.6.2 *Standardization of Simple Cyanide Stock Solution*—(See 8.6.1.) Once a month standardize against the primary standard silver nitrate titrant using 10 mL of KCN stock solution and rhodanine indicator.

8.6.3 *Complex Cyanide Solution, Stock* 1.0 g/L CN—Dissolve 0.2109 g of potassium ferricyanide, $K_3Fe(CN)_6$, or 0.2706 g of potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$, in distilled water. Add five pellets of NaOH, mix well and dilute to 100 mL. This solution must be stored in the dark, and preferably in a dark bottle.

8.6.4 *Thiocyanate Solution, Stock Potassium Thiocyanate, KSCN,* 1 g/L CN— Dissolve 0.3735 g of potassium thiocyanate in distilled water. Add about five pellets of NaOH, mix well and dilute to 100 mL.

8.6.5 All stock solutions in 8.6.1 through 8.6.4 should be prepared fresh every month. One millilitre of stock solutions (8.6.1 through 8.6.4) ≡ 1 mg CN.

8.6.6 *Daily Working Standards,* 100 µg/L CN. With a micropipette take 100 µL of stock solution and dilute to 1 L with 0.02 *M* NaOH. Other working standards could be prepared as desired for different concentration ranges.

8.7 *Acid Digestion Mixture*:

8.7.1 *Acid Mixture for Total Cyanide Plus Thiocyanate*—Prepare 1 L by dissolving 200 mL of (85 %) orthophosphoric acid, 40 mL of (50 %) hypophosphorus acid, and 2 g of sulfamic acid in water.

8.7.2 *Acid Mixture for ~~Total Cyanide and~~ Acid Dissociable Cyanide or Acetate Buffer Used*—As directed in 8.7.1 but without hypophosphorus acid.

8.7.3 *Acetate Buffer*— Dissolve 410 g of sodium acetate trihydrate in 500 mL of water. Add glacial acetic acid to yield a pH of 4.5 (about 500 mL).

8.7.4 *Acid Mixture for Partial Acidic Irradiation (Before the Total Cyanide Alkaline UV Irradiation)*— Dissolve 40 mL of orthophosphoric acid and 2 g of sulfamic acid in water and dilute to 1 L.

8.8 *Diluent (Added to the Sample Stream via the Manifold)*:

8.8.1 For the acid dissociable cyanide and total cyanide plus thiocyanate the diluent is water.

8.8.2 For total cyanide the diluent is 0.25 M NaOH (10 g/L).

8.8.3 *Diluent with Sodium Borohydride* —Similar to 8.8.2, but also contains 0.35 g of $NaBH_4$ per litre (which is equivalent to 2 mL of sodium borohydride VenMet solution[8]). For treatment of interferences, this diluent should be used instead of the above diluents, in all these automated measurements (See 6.4, 6.5, 6.6, and 6.7).

8.9 *Reagents for Color Development* :

8.9.1 *Phosphate Buffer Solution,* 0.6 *M* (pH ~ 4.2)—Dissolve 83 g of sodium phosphate monobasic in water, dilute to 1 L.

~~[7] Supporting data are available from ASTM Headquarters. Request RR:D19-1143.~~

[7] *Reagent Chemicals, American Chemical Society Specifications* , American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[8] VenMet solution, a stable aqueous solution of 12 % sodium borohydride, by Morton Thiokol Inc., 150 Andover St., Danvers, MA 01923–1428, has been found suitable for this purpose.

8.9.2 *Chloramine-T Solution, 5 % Stock Solution*—Carefully dissolve 5.0 g of chloramine-T in distilled water and adjust volume to 100 mL. Prepare weekly and store in the dark.

8.9.2.1 *Chloramine-T Daily Working Solution, 0.4 %*—Dilute 20 mL of the stock to 250 mL.

8.9.3 *Pyridine-Barbituric Acid Color Reagent*—Place 15 g of barbituric acid in a 1-L flask; add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. After dissolution add 15 mL of HCI (sp gr 1.19), mix and let cool at room temperature, then dilute to the mark. Keep in a brown glass bottle and store in the dark. The reagent is stable for more than three months.

9. Hazards

9.1 **Precaution**—Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations should be done in the hood so that any HCN gas that might escape is safely vented.

9.2 If a cyanide solution or a cyanide-containing waste is spilled on the skin, wash it off with water. If it is splashed in the eyes, irrigate the eyes with running water for 15 min and call a physician at once. If swallowed, call a physician and give inhalations of amyl nitrite for 15 to 30 s every 15 min for 1 h. When the patient is conscious, give emetics (warm salt water) until the vomit fluid is clear.

9.3 **Warning**—Many of the reagents used in these test methods are highly toxic. These reagents and their solutions must be disposed of properly.

10. Sample Handling and Preservation

10.1 Collect the sample in accordance with Practice D 3370.

10.2 Samples should be collected in dark polyethylene or glass containers, and analyzed as soon as possible.

10.3 If the sample cannot be analyzed immediately, and does not contain sulfides or oxidizing materials, add sodium hydroxide (pellets or concentrated solution) to raise the pH to ≥12 for preservation.

10.4 Cover the container tightly and store in a dark, cool place, at about 5°C.

10.5 The use of dark containers and storage in a dark place is to minimize sample exposure to UV irradiation, otherwise photodecomposition of cyanide complexes may occur. The photodecomposition of iron complexes increases the free cyanide significantly and alters the relative cyanide species distribution in the samples.

10.6 If the sample contains sulfides or oxidizing agents, treat as prescribed in 6.3 and 6.4 respectively prior to preservation with sodium hydroxide.

10.7 Test for the presence of sulfides by placing a drop of the sample on a strip of lead acetate paper moistened with the phosphate buffer. Darkening of the test paper indicates the presence of sulfide. Presumably the presence of sulfide indicates the absence of oxidizing agents.

10.8 Test for presence of oxidizing agents by placing a drop of the sample on a strip of potassium iodide-starch paper moistened with the phosphate buffer. Appearance of a dark bluish color indicates the presence of oxidizing substances.

10.9 If the sample contains oxidizing agents, treat as prescribed in 6.4 or, better, analyze immediately.

11. Procedure for Total Cyanide

11.1 Acidification is made after the alkaline UV irradiation as shown in Fig. 1. However, for treatment of some interferences modifications in the manifold should be made in accordance with Section 6 and Fig. ~~3.~~ 2.

11.2 *System Preparation and Warm Up (20 min)*—Start the pump using water instead of reagents.

11.3 *Distillation Ratio, 10 to 20 %* :

11.3.1 Measure the cold liquid volume flowing through the thin film distillation unit, by collecting the water from the waste trap in a measuring cylinder for 10 min. This volume should be about 26 mL according to the described manifold.

11.3.2 Turn on the UV irradiator (with the borosilicate coil) and activate the tickler if needed.

11.3.3 Turn on the variable transformer to heat the aluminum bar. Wait about 12 min to reach a stable temperature. The temperature should be monitored by the dial thermometer in the aluminum bar well (about 125°C).

11.3.4 Collect the hot liquid from the waste trap for 10 min. Wait until it cools to room temperature, then measure the volume. This volume should be around 21 to 24 mL, otherwise temperature adjustment by the Variac controls is necessary.

11.3.5 The distilled volume (the difference between the cold volume and the hot volume) should be about 2 to 5 mL to yield a distillation ratio of 10 to 20 %.

11.3.6 Alternatively, the UV distillation unit could be used, especially in presence of interferences (6.7 and 7.5, and Fig. 2). In this case, higher distillation ratios, if desirable, could be achieved without disturbing the system.

11.4 *Standard Calibration*—Calibration is linear up to 5 mg/L when using a 15 mm flow cell, and up to only 500 µg/L with a 50 mm flow cell. The following steps are recommended for the working range of 0 to 100 µg/L.

11.4.1 Run the system with the reagents, no samples or CN standards. Wait about 12 min for the reagents to flow through the colorimeter flow cell.

11.4.2 Place, successively, in the sampler tray four cups of 50 µg/L CN standards, two cups of 100 µg/L CN standard, two cups of 100 µg/L CN complex standard (ferro- or ferricyanide), and two cups of water. Start the sampler.

11.4.3 It takes about 12 min for the first peak to appear. Adjust the colorimeter standard calibration control so that at the plateau of the 50 µg/L CN peak reads 50 (or the assigned value) on the chart recorder. Use the next peak for exact adjustments. The third and fourth peaks should prove to be satisfactory.

11.4.4 The next two peaks belong to the 100 µg/L CN and should read 100 (or as assigned), within the experimental variation.

11.4.5 The last two peaks correspond to the strong complex cyanide and should give a concentration of 100 µg/L CN. If those peaks are lower than expected then the UV irradiation may not be effective and should be checked.

11.4.6 The distilled water in the last two sample cups should not give any response, and the baseline should return to zero; otherwise, minor adjustments should be made.

11.5 *Analysis of Field Samples*:

11.5.1 The system is now ready and calibrated to measure total cyanides. The samples have been checked and treated for interferences, if found (as in Section 6).

11.5.2 Sludge, sediment, or soil samples need to be homogenized thoroughly in a heavy-duty blender or an ultrasonic disruptor. Proper dilutions should be made according to their cyanide level, then fed into the system.

11.5.3 Fill an identified cup or two if analyzing samples in duplicate and load the sample tray.

11.5.4 Follow all other good quality control practices and include check cyanide standards and distilled water as necessary.

11.5.5 Avoid introducing samples containing very high cyanide concentrations without proper dilution. Otherwise, the peaks exceed the recorder range (off-scale) and the system may need a suitable wash (see 14.1) to return to baseline. Reanalyze any samples affected by carry-over contamination.

11.5.6 Results are read directly from the recorder chart (linear absorption), or from a calibration curve in cases where the working concentration range is high and the response is not ideally linear.

11.6 *Shut Down Steps and Routine Wash*:

11.6.1 After the last sample analysis is completed keep the pump on and turn off the recorder, variable transformer, and UV irradiator.

11.6.2 *Sodium Hydroxide Wash*—Place all the reagent and sample lines in 0.02 *M* NaOH for 10 min to rinse the system.

11.6.3 *Water Wash*—Place all reagent and sample lines in water for 15 to 20 min.

11.6.4 Turn off the pump, then release the platen and pump tubes.

12. Procedure for Acid Dissociable Cyanide

12.1 All the steps prescribed for determining total cyanide apply for the acid dissociable cyanide, whether strong acid mixture or weak acidic acetate buffer is used. No UV radiation, however, is employed.

12.1.1 The UV irradiator must be turned off. The unit can be bypassed completely; this will reduce the run-time approximately 5 min.

12.1.2 The cold and hot volumes (for the distillation ratio) collected for 10 min will be approximately 26 and 21 to 24 mL, respectively.

12.2 Alternatively, if the UV distillation unit is used, the irradiation coil must be bypassed and only the opaque small heating coil is used for distillation (7.4 and Fig. 2).

12.3 A separate chemical standard calibration is necessary. The system must be recalibrated before determination of acid dissociable cyanide. No response will be noted for the strong cobalt-cyanide complex or thiocyanate. Ferro- and ferricyanide complexes may give a small response due to some decomposition. The response should be <5 % of the total cyanide employing the UV irradiation.

12.4 Specific standardization and calibration procedures for acid dissociable cyanide shall be followed, similar to total cyanide (Section 11), as well as all other QC/QA steps and actions must be followed (Section 17).

13. Procedure for Thiocyanate

13.1 The steps are similar to the total cyanide procedure, with the following exceptions:

13.1.1 Acidification is made before UV, and the acid mixture contains hypophosphorus acid to prevent oxidation by UV irradiation.

13.2 The distillation cold and hot volumes would be similar to acid dissociable and total cyanide, that is, 26 and 21 to 24 mL, respectively.

13.2.1 The quartz coil is used (instead of the borosilicate coil) in the UV irradiation to break down the thiocyanate in addition to all the complex cyanides. Thus this measurement will be for the total cyanide plus thiocyanate.

13.3 Specific standardization and calibration procedures shall be followed, similar to total cyanide (Section 11), as well as all other QC/QA steps and actions must be followed (Section 17).

13.4 The thiocyanate, as CN, is calculated by difference: thiocyanate = total cyanide plus thiocyanate − total cyanide.

13.5 To obtain thiocyanate as SCN, multiply by the factor 2.23.

14. Maintenance

14.1 *Daily*—After use wash the system for 10 min with 0.02 *M* NaOH, followed by 15 to 20 min with water.

14.2 *Monthly*:

14.2.1 Before changing pump tubes, wash the UV quartz coil and borosilicate glass using both acid tube and sample pump tube with 5 % HCl for 10 min, 10 min with 0.02 *M* NaOH, and 10 min more with distilled water.

14.2.2 Now, change all pump tubes.

14.2.3 Change any transmission tubing that appears to be dirty, colored, or sticky, as well as any loose sleeves.

14.3 Routine periodic maintenance for all automated continuous flow modules according to manufacturer manuals should be followed, including pump lubrication.

15. Trouble Shooting

15.1 *Contamination*— Samples containing high concentrations of cyanide may result in system contamination, as noted by persistent color in the glass coils and the failure of the recorder tracing to return to baseline.

15.1.1 Rinse the system with the following wash solutions until the color is removed from the system: (*a*) 1.0 *M* NaOH, (*b*) HCl acid, 5 % by volume, then (*c*) with water.

15.2 *Waste Trap Failure*—Excessive amounts of gases may escape from the waste trap and interrupt the flow pattern. This rarely occurs, and is the result of evolution of gases from samples extremely high in cyanide or carbonate.

15.2.1 The waste trap is designed to be self-filling, and should correct itself in a few minutes.

15.2.2 Verify that the system is back to normal by checking the distillation ratio (see 11.4.2).

15.2.3 Repeat the analysis of the samples affected by improper operation of the waste trap.

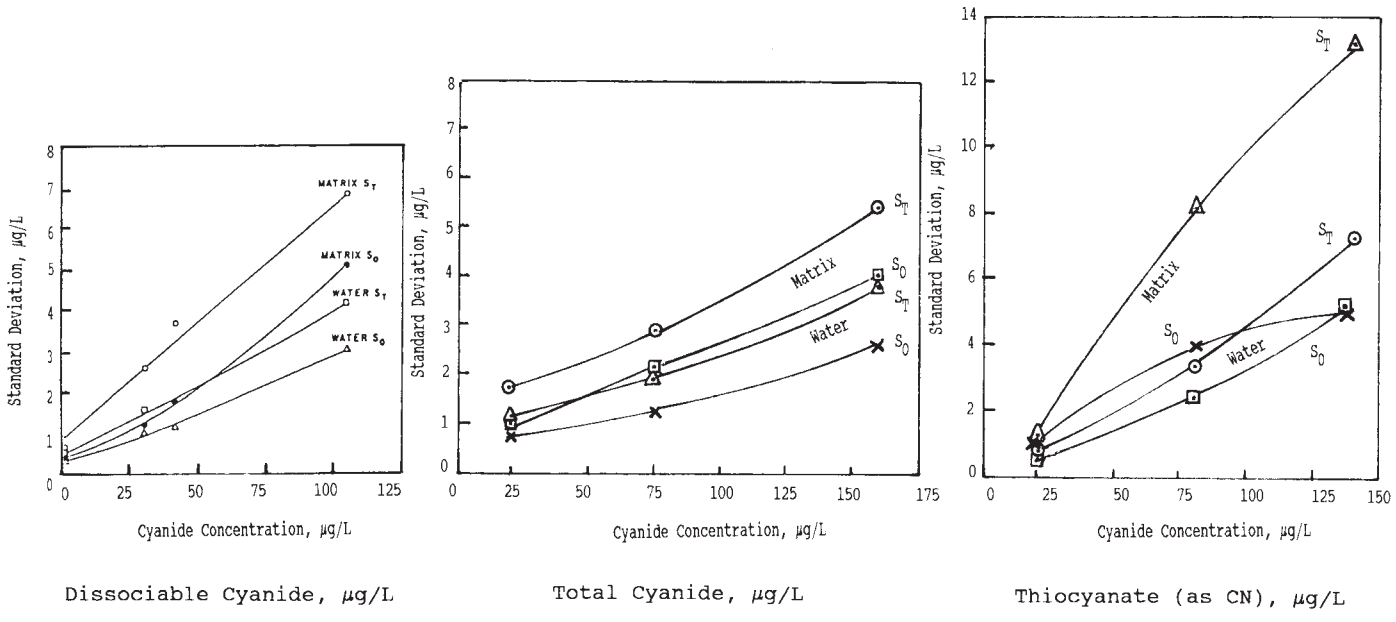
16. Precision and Bias [9]

16.1 The collaborative studies for performance evaluation of these test methods were conducted according to Practice D 2777.

16.1.1 Three collaborative studies were conducted for the three parameters of total cyanide, acid dissociable cyanide, and thiocyanate. Eight laboratories from the United States and Canada participated with eleven operators. The concentration levels chosen were between zero and 200 µg/L. Duplicate analyses were performed in each run and replicated for four or three days, thus about 80 observations were obtained for each concentration. Other than reagent water, different field sample matrices were used, that is, drinking water, natural ground well water, lake water, river water, raw sewage, sludge, treated effluent, and industrial waste.

16.2 *Precision*—The overall precision, S_T, and the single operator precision, S_O, show that the standard deviation increases with concentration, and somewhat higher in field samples than water. This was true for all concentration levels as presented in Fig. 5 for total cyanide, acid dissociable cyanide, and thiocyanate, respectively. The graph is drawn by connecting the calculated standard

[9] Supporting data are available from ASTM Headquarters. Request RR:D19-1143.



where:

S_T = overall standard deviation,
S_o = single-operator standard deviation,
Water = reagent distilled water, and
Matrix = selected field water matrixes.

FIG. 5 Precision

deviations at the different concentrations. Alternatively, the best regression equation that fits the calculated values could be represented by the following equations for the respective three parameters:

16.2.1 *Total Cyanide*:

water	$S_T = 0.0209X + 0.6409$
	$S_O = 0.0131X + 0.4498$
selected matrices	$S_T = 0.0269X + 1.0406$
	$S_O = 0.0191X + 0.6591$

where:

X = concentration, µg/L.

16.2.2 ~~D~~*acid dissociable Cyanide*:

water	$S_T = 0.0337X + 0.5461$
	$S_O = 0.0254X + 0.2845$
selected matrices	$S_T = 0.0585X + 0.9780$
	$S_O = 0.0468X + 0.1803$

where:

X = concentration, µg/L.

16.2.3 *Thiocyanate*:

water	$S_T = 0.0559X - 0.4198$
	$S_O = 0.0384X - 0.3062$
selected matrices	$S_T = 0.0963X - 0.1847$
	$S_O = 0.0323X - 0.6785$

where:

X = concentration, µg/L.

16.3 *Bias*—Evaluation of bias from the data obtained from the round robin collaborative studies are presented in Table 1, Table 2, and Table 3 for total cyanide, acid dissociable cyanide, and thiocyanate, respectively.

16.3.1 Recoveries of known amounts of total cyanide, acid dissociable cyanide and thiocyanate (as cyanide) from water samples yielded good values, 97 % or better.

16.3.2 Recoveries from field sample matrices were within 94 % for total cyanide and thiocyanate, and within 92 % for acid dissociable cyanide. It should be mentioned that in other studies recoveries of acid dissociable cyanide were sometimes lower and probably due to some complexing factors in those matrices, making some cyanides not available for such measurement.

16.4 It should be recognized that this data may not apply to other matrices than those tested.

17. Quality Control (QC)/Quality Assurance (QA)

17.1 These specific terms are for quality control objectives and are explained and defined as follows.

17.1.1 *Calibration Standards*—These standard solutions are of known concentration either purchased from an external source or prepared in-house from materials of known purity or concentration, or both, used to calibrate instrumentation.

17.1.2 *External Calibration Check* —Analyze an independent standard solution, such as a certified reference material of known purity and concentration either obtained from the National Institute of Standards and Technology or other reputable supplier other than the laboratory's usual source. This analysis is carried out periodically to check the accuracy of the laboratory's routine calibration standard solutions.

17.1.3 *Matrix Spike*— This term describes the addition of a known concentration of analyte to a sample representing a specific matrix for the purpose of evaluating interference and recovery from matrix components.

17.1.4 *Method Blank*— This term describes the reagent water (see Specification D 1193), either known to be free of the constituent of interest or containing only a low, known concentration of the constituent of interest not exceeding five times the

TABLE 1 Determination of Bias—Total Cyanide

Amount Added, µg/L	Mean Recovery, $\bar{X}$, µg/L	±Bias	± Bias, %
20	19.9	−0.1	−0.3
75	75.3	+ 0.3	+ 0.3
160	159.4	−0.6	−0.4
Field Matrices			
20	18.8	−1.2 [A]	−6.2
75	73.9	−1.1 [A]	−1.5
160	157.6	−2.4 [A]	−.5

[A] Bias significant at the 5 % level.

TABLE 2 Determination of Bias—Dacid dissociable Cyanide

Amount Added, µg/L	Mean Recovery, $\bar{X}$, µg/L	±Bias	± Bias, %
1	1	zero	zero
30	30.3	+ 0.3	1.0
41	42.3	+ 1.3 [A]	3.2
103	105.4	+ 2.4 [A]	2.3
Field Matrices			
1	1	zero	zero
30	27.7	−2.3 [A]	−7.7
41	39.1	−1.9 [A]	−4.6
103	101.7	−1.3	−1.3

[A]Bias significant at the 5 % level.

TABLE 3 Determination of Bias—Thiocyanate

Amount Added, µg/L	Mean Recovery, $\bar{X}$, µg/L	±Bias	± Bias, %
20	20	zero	zero
80	78	−2 [A]	−2.4
140	138	−2 [A]	−1.7
Field Matrices			
20	19	−1 [A]	−6.2
80	79	−1 [A]	−1.5
140	144	+ 4 [A]	−1.5

[A]Bias significant at the 5 % level.

estimated minimum detection level. The purpose of the analysis of the method blank is to confirm that the reagents or analytical system, or both, do not contribute a measurable amount of the constituent of interest during analysis of routine samples, or if they do, to determine what that contribution is.

17.1.5 *Quality Control Sample*—This term describes a sample of known concentration and composition that is taken through the entire analytical procedure to determine whether the analytical system is in control. The sample can be a certified reference material obtained from an outside source or prepared in-house from materials of known purity and concentration. The quality control (QC) sample shall be prepared from material that sufficiently challenges the test. Alternatively, the QC sample may be a fully characterized real sample of the matrix that is typically analyzed.

17.1.6 *Set of Samples*— This term describes a group of 20 or fewer samples of the same matrix type that are being analyzed for essentially the same components.

17.2 The main quality control requirements are described as follows:

17.2.1 Verification of system calibration and of control at zero analyte concentrations and analysis of system blanks;

17.2.2 Verification of control at representative analyte concentration and quality control samples;

17.2.3 Initial demonstration of proficiency; and,

17.2.4 Replicates are required for specific proof and assessment of precision as well as assessment of bias.

17.2.5 For general discussion of quality control and good laboratory practices, see Practice D 5789.

17.3 *Calibration of the Cyanide Automated System*:

17.3.1 *Calibration Curve*—For initial calibration use five concentration levels, in duplicates (10, 25, 50, 100, 150-µg/L), and include one blank or more. Also, it is useful to include standards of parameters not intended to be measured, such as iron or cobalt complexes for calibration and analyses of acid dissociable cyanide, to assure that they are not measured.

17.3.2 *Calibration Check*—A single calibration standard, 100 µg/L or 50 µg/L (or better in duplicate) is required at the start of each day and for every set of sample. Internal standards can be used, however, this should be checked periodically with external certified standards. This calibration check must be within 10 % of the initial calibration, otherwise recalibration should be performed.

17.3.3 *Method Blank*— At least one method blank shall be analyzed with each set of samples. The blank result shall be below 0.5 µg/L, otherwise recalibration should be performed.

17.4 *Quality Control Samples*—These samples verify control at the representative analyte concentration. Ongoing QC samples are necessary for each sample matrix, at least one per each sample set.

17.4.1 The QC sample can be a certified reference material from an outside source or prepared from known purity and concentration. Alternatively, the QC sample may be a fully characterized real sample of the matrix that is typically analyzed.

17.5 *Initial Demonstration of Proficiency* :

17.5.1 A successful demonstration to confirm that each method user is capable of generating meaningful data, by statistic comparison to the precision and bias data of the collaborative testing presented in Section 16.

17.5.2 Analysis of at least seven replicates is required, for each intended parameter, namely acid dissociable cyanide, total cyanide, and thiocyanate. A concentration of 20 to 100 µg/L in reagent water is proposed. Other choices could be used if in accordance to Practice D 5789.

17.5.3 The standard deviation obtained from the analyst proficiency demonstration then is compared to the acceptable control limits (*CL*) for precision, calculated from the collaborative study data (see Table 4).

$$CL = \chi \pm 3\, S_T \tag{1}$$

17.5.4 *Calculation of Maximum Acceptable Limits for Precision*—The maximum acceptable standard deviation (S_m) is based on *F*-test at the 1 % significance level and the number of replicates, according to equation:

$$S_m = \sqrt{F_{0.99}}\,(S_o) \tag{2}$$

17.5.5 *Acceptable Limits for Bias* —The limits for the mean concentration (X) of n replicate recovery measurements are as follows:

$$X \pm t_{0.99}\ \sqrt{S^2_t - \frac{(n-1)\,S^2}{n}} \tag{3}$$

where:
$t_{0.99}$ = Student's t for a two-tailed test at the 99 % confidence level at $N - 1$ df, and
n = the number of laboratories that provided usable data in the collaborative study (=8).

See Table 4 for the acceptable limits.

17.6 *Assessment of Precision*—The replicate analysis is to ensure that the test method is performing properly and the assessment of precision should be done for each sample set.

17.6.1 Spiked replicates could be used, especially where nondetects are frequent.

17.6.2 The relative standard deviation (*RSD*) from duplicate results is as follows.

$$RSD\% = \frac{R}{\overline{X}}\sqrt{\frac{100}{2}} \tag{4}$$

where:
R = range of duplicates, and
X = average concentration.

17.6.2.1 Acceptable relative standard deviation are suggested to be up to 10–15 % for low cyanide levels, and ≥ 20 % for higher levels. Thiocyanate determination by this automated method is made by subtraction, thus the relative standard deviation could be somewhat higher.

17.6.3 The analyst and laboratory also should construct control charts and develop their own acceptable ranges as described in Guide D 3856 and Practice D 4210.

17.7 *Assessment of Bias*—To address properly matrix effects, samples are spiked with the analyte, according to Guide D 5788 with a frequency of 5 % or more.

17.7.1 The bias is calculated as follows.

$$Recovery,\ \% = \left(\frac{A-B}{C}\right) 100 \tag{5}$$

TABLE 4 Quality Control Acceptable Ranges

Parameter	Spike µg/L	Proficiency Demonstration: Acceptable Standard Deviation (Precision), Max	Proficiency Demonstration: Acceptable Recovery (Bias)	QC Acceptable Range ($CL = \times \pm 3\ S_T$): Reagent Water	QC Acceptable Range ($CL = \times \pm 3\ S_T$): Sample Matrix
Dissociable cyanide:	30	2.30	(30 ± 4.24) 25.76 to 34.24	(30 ± 3 × 1.56) 25.32 to 34.68	(30 ± 3 × 2.73) 21.81 to 38.19
	100	6.20	(100 ± 10.11) 89.89 to 110.11	(100 ± 3 × 3.92) 88.24 to 111.76	(100 ± 3× 6.83) 79.52 to 120.48
Total cyanide:	100	3.86	(100 ± 7.62) 92.38 to 107.62	(100 ± 3 × 2.73) 91.81 to 108.19	(100 ± 3× 3.73) 88.81 to 111.19
Thiocyanate:	100	7.77	(100 ± 13.92) 86.08 to 113.92	(100 ± 3 × 5.17) 84.49 to 115.5	(100 ± 3× 9.21) 72.37 to 127.63

where:
A = Concentration found in spiked sample,
B = Concentration found in unspiked sample, and
C = Concentration found in added spike.

17.7.2 Recoveries of 90 % or better is expected for cyanide and 80 % for thiocyanate. The analyst and laboratory should construct control charts and develop performance acceptable ranges.

17.8 *Maintenance of Interlaboratory Traceability*—Periodic analysis of certified reference material (CRM) and participation in interlaboratories proficiency studies are used to provide external quality assurance evaluation. The results become indexed and traceable to national standard of performance.

17.8.1 These proficiency studies should be conducted on a quarterly basis.

18. Keywords

18.1 automated methods; cyanide; acid dissociable; thiocyanate; waste water

APPENDIXES

(Nonmandatory Information)

X1. SULFIDE INTERFERENCE

TABLE X1.1 Reaction of Sulfide with Cyanide at pH > 12 and Formation of Thiocyanate
CN^- = 100 µg/L (as KCN), $S^=$ = 10 g/L (as Na_2S)

	Time									
	0 h		2 h		4 h		6 h		24 h	
	D [A]	*T* [B]	*D*	*T*	*D*	*T*	*D*	*T*	*D*	*T*
CN^- concentration, µg/L	100	100	87	101	85	102	84	103	77	102
CN^- transformed to SCN^-	...		13 %		15 %		16 %		23 %	
	2 days		3 days		1 week		2 weeks		3 weeks	
CN^- concentration, µg/L	70	99	67	95	63	98	46	101	39	100
CN^- transformed to SCN^-	30 %		33 %		37 %		54 %		61 %	

[A] *D* = ~~D~~acid dissociable cyanide.
[B] *T* = Total cyanide plus thiocyanate.

X2. NITRATE-NITRITE INTERFERENCE

X2.1 There is no interference from nitrate or nitrite with acid dissociable cyanide, whether with synthetic preparations or field samples.

X2.2 Nitrite interferes significantly with total cyanide measurements. Nitrate does not interfere unless reduced to nitrite (it is possible that nitrate may be reduced in presence of hypophosphorus in the acid mixture, or some reducing substances in field samples).

X2.3 Nitrite interference is positive under acidic conditions and not noticeable with synthetic samples up to a concentration of about 20 mg/L. Whereas with alkaline UV irradiation the nitrite interference is negative and significant at lower concentrations (see Table X2.1). The interference is greater with field samples.

X2.4 The nitrite interference is more pronounced in presence of strong reducing agents such as arsenite or sodium borohydride. With field samples the interference is significant even at 1 mg/L nitrite and rapidly increases to off scale in acidic conditions and down to zero with alkaline UV at 10 mg/L and higher (see Table X2.1 and Table X2.2).

X2.5 *Sulfamic Acid Treatment:*

X2.5.1 The use of urea and sulfamic acid to remove nitrous acid or nitrite is prescribed in analytical reference **(7, 8)**. The following equations represent the two reactions respectively:

$$2H^+ + 2NO_2^- + CO(NH_2)_2 \rightarrow 2N_2 + CO_2 + 3H_2O$$

$$H^+ + NO_2^- + O{\cdot}SO_2NH_2^- \rightarrow N_2 + HSO_4^- + H_2O$$

TABLE X2.1 Nitrite Interference with Total Cyanide and Treatment with Sulfamic Acid

Conditions	Nitrite, mg/L (Added to 100 µg/L Cyanide as KCN)				
	10	25	50	75	100
	(Cyanide recovered, µg/L)				
Acidic UV:					
No sulfamic	102	108	125	140	off scale
With Borohydride & No sulfamic	102	110	135	off scale	off scale
With sulfamic	99	100	98	96	99
With sulfamic & Borohydride	101	101	97	98	101
Alkaline UV:					
No sulfamic	70	65	61	58	58
With Borohydride & No sulfamic	9	2	1	1	1
With sulfamic	98	101	95	94	97
With sulfamic & Borohydride	96	99	103	89	94

TABLE X2.2 Nitrate-Nitrite Interference with Total Cyanide Plus Thiocyanate Measurement in Presence and Absence of Arsenite

Sample	Interferent, mg/L							
	0	1	5	10	15	25	50	100
	(Total Cyanide Result, µg/L)							
No. Arsenite:								
Raw Sewage + NO_3	40	38	39	40	50	64	81	110
Treated Effluent + NO_2	27	26	28	28	35	39	45	58
Arsenite Present:								
Raw Sewage + NO_3	62	66	100	off-scale	...	...	...	off-scale
Raw Sewage + NO_2	62	85	off-scale	...	...	...	...	off-scale

Several attempts have been made to evaluate the effectiveness of both substances. Urea did not seem to be effective under the system experimental conditions. Sulfamic acid has been effective in removing both the positive and negative interferences of nitrite (see Table X2.1, Table X2.2, and Table X2.3).

TABLE X2.3 Effect of Original Nitrate-Nitrite Content and Sulfamic Acid on Total Cyanide Plus Thiocyanate Measurement in Some Waste Treatment Plant Samples

Treatment Plant Sample	Cyanide, µg/L	Total CN^- + Sulfamic Acid	NO_3^-/NO_2^- Content, mg/L
Plant I:			
Raw	98	80	3.5
Effluent BC [A]	24	12	9.0
Effluent AC [B]	55	22	9.7
Plant II:			
Raw	86	84	2.0
Effluent BC	44	44	0.7
Effluent AC	71	70	1.0
Plant III:			
Raw	62	60	1.5
Effluent BC	19	11	3.6
Effluent AC	31	25	2.0
Plant IV:			
Raw	21	15	2.3
Effluent (1)-BC	12	5	7.1
Effluent (2)-BC	17	9	7.7
Effluent AC	35	14	7.7
Plant V:			
Raw	10	8	0.5
Effluent BC	23	6	15.0
Effluent AC	41	7	13.4
Plant VI:			
Raw	69	53	2.1
Effluent BC	33	9	11.3
Effluent AC	...	...	...

[A] BC—Before chlorination.
[B] AC—After chlorination.

X2.5.2 It was found that a sulfamic acid concentration of 2 g/L (of acid mixture) gives good cyanide recoveries in the presence of 50 to 100 mg/L nitrite.

X3. ALDEHYDE INTERFERENCE

See Table X3.1

TABLE X3.1 Recovery of Cyanide from Aldehyde Interference Using Ethylene Diamine

Test Solution	3.5 % Ethylene Diamine per 100-mL Test Solution, mL															
	0		1		2		4		6		8		10		12	
	D [A]	*T* [B]	*D*	*T*	*D*	*T*	*D*	*T*	*D*	*T*	*D*	*T*	*D*	*T*	*D*	*T*
KCN, 100 µg/L	100	100	...	...	106	102	103	101	...	...	111	110	...	...	111	110
KCN + Formaldehyde, 5 mg/L	46	60	72	92	75	99	76	100	83	113	85	112	...	...	...	...
KCN + Formaldehyde, 10 mg/L	31	48	70	110	70	112	70	113	70	112	69	118	68	117	71	119
KCN + Formaldehyde, 25 mg/L	10	26	43	100	42	104	44	111	39	103	38	100	42	112	42	114
KCN + Formaldehyde, 50 mg/L	5	20	22	88	39	106	27	103	28	109	17	102	30	113	28	108
KCN + Formaldehyde, 100 mg/L	1	14	7	51	11	66	12	73	13	83	14	95	15	95	15	99

[A] *D* = Dissociable Cyanide, µg/L.
[B] *T* = Total Cyanide, µg/L.

REFERENCES

(**1**) Kelada, N. P.," Automated Direct Measurements of Total Cyanide Species and Thiocyanate, and their Distribution in Wastewater and Sludge," *J. WPCF*, Vol 61, March, 1989.

(**2**) Kelada, N. P., ~~et al, *In-Line Continuous Thin Film*~~ "*Cyanide Speciation Utilizing UV Irradiation and* Distillation ~~*System*~~, ~~U.S. Patent 4265857, May 5, 1981.~~ Within a Single Automated Module," Pittsburgh Converence, Atlanta, George, 1997.

(**3**) Kelada, N. P., et al, ~~*Methods and Apparatus for Measuring Cyanide*, U.S. Patent Application #859049, 1986.~~ "Randol Gold Forum," p 385, 1992 (Randol Int., Golden, Colorado).

(**4**) Goulden, P. D., Afghan, B. K., and Brooksbank, P.," Determination of Nanogram Quantities of Simple and Complex Cyanides in Water," *Analytical Chemistry* , Vol 44, p. 1845, 1972.

(**5**) Kelada, N. P., Lordi, D. T., and Lue-Hing, Cecil," Cyanide Species Methodology in Water, Wastewater, and Sediments," The Metropolitan Sanitary District of Greater Chicago, R & D Dept., Report No. 77-5, 1977. Also appears in *Advances in Automated Analysis*, Vol 2, Technicon International Congress, 1977.

(**6**) Kelada, N. P., Lue-Hing, Cecil, and Chavich, J.," Cyanide-Thiocyanate Speciation and Removal of Thiocyanate and Other Interferences," paper presented at the Conference on Cyanide and the Environment, Tucson, AZ, 1984.

(**7**) *Standard Methods for the Examination of Water and Wastewaters* , Fifteenth Edition, APHA, AWWA and WPCF, New York, NY, 1980.

(**8**) Kruse, J. M., and Mellon, M. G.," Colorimetric Determination of Cyanide," *Sewage Industry Wastes*, Vol 23, 1951, p. 1402.