Designation: D 4374 – 00

Standard Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, 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, 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*, % =

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

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

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[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. 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).

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).

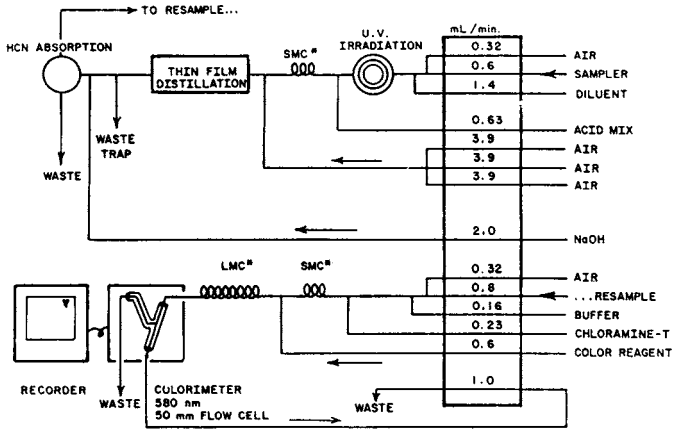
5. Significance and Use

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.



* 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

6.3 *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.

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 ($SnCl_2$), 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 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 7.6, 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

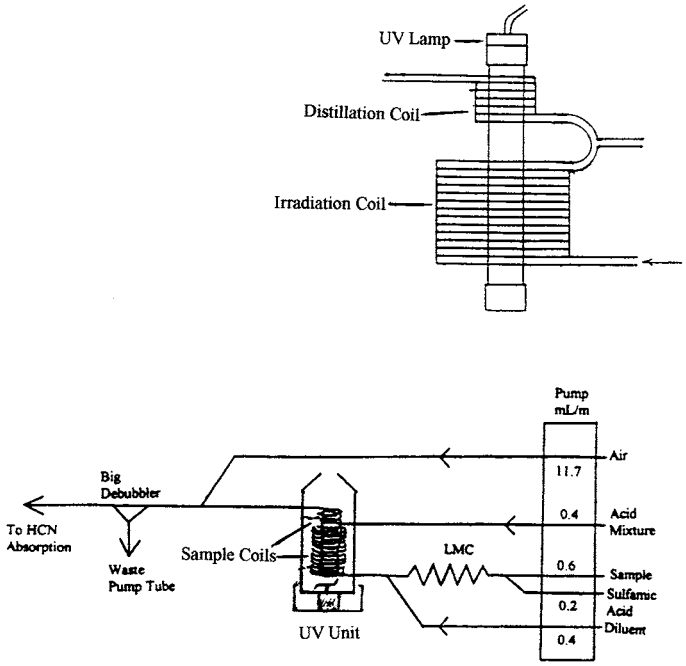


FIG. 2 Partial Manifold for Total Cyanide (Before Color Development)

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 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 (7.6 and Fig. 2) and addition of acid mixture before the 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. 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*:

7.4.1 The unit is made of borosilicate glass tubing and a schematic is presented in Fig. 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.

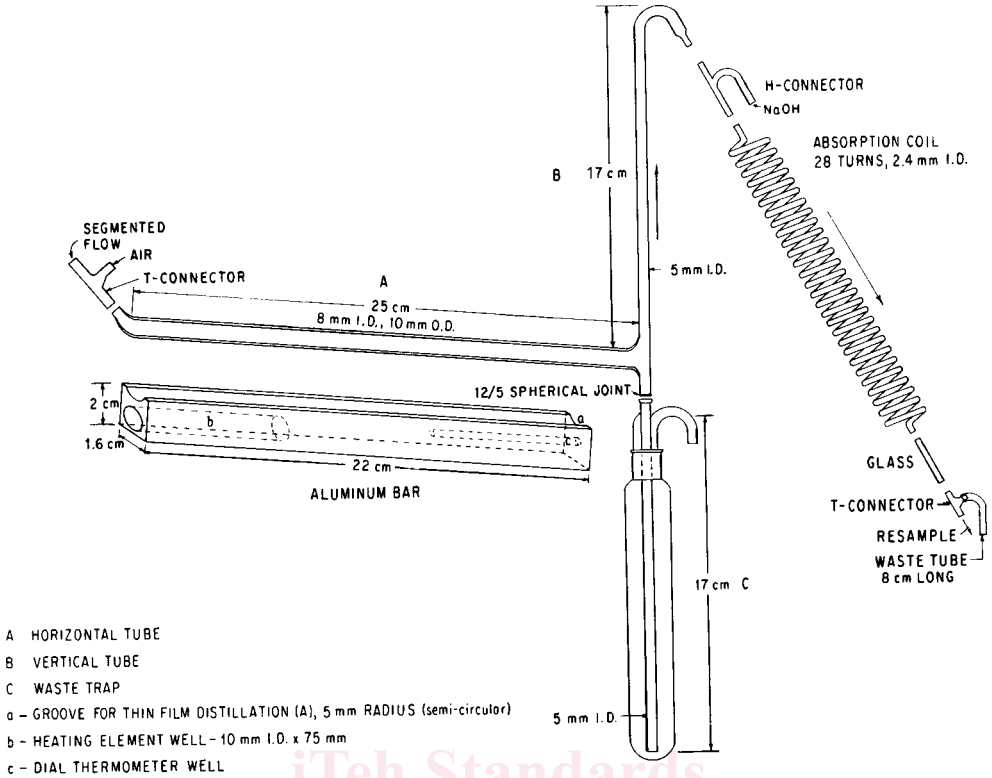


FIG. 3 Continuous Thin Film Distillation Unit

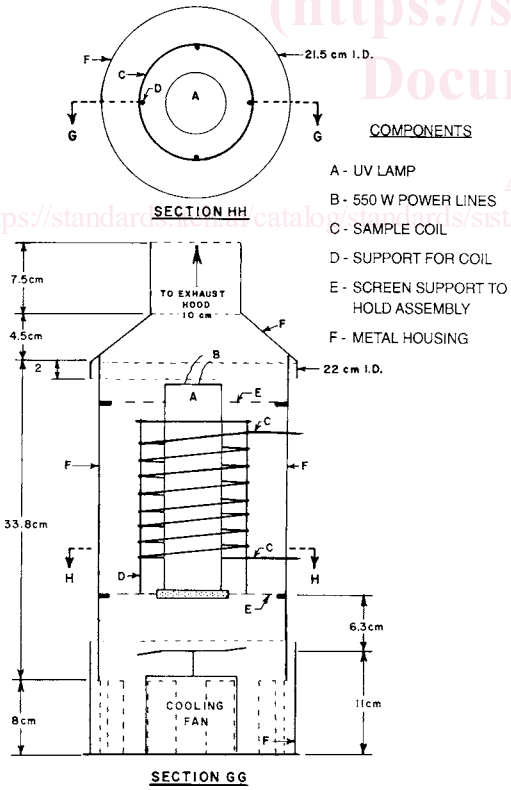


FIG. 4 Ultraviolet Irradiation Unit (Lamp, Coil, and Housing)

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) 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.

7.5 *Gas Absorber*— Absorption of HCN gas is achieved by forcing the gas mixture and 0.02 *M* NaOH solution through an absorption glass coil, 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*:

7.8.1 The air flow (from the three pump tubes) and the segmented flow from the UV irradiator should lead directly

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

(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.

7.8.2 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.

7.8.3 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 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 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] *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.