Designation: D6888 − 16 (Reapproved 2023)

Standard Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection[1]

This standard is issued under the fixed designation D6888; 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 This test method is used to determine the concentration of available inorganic cyanide in an aqueous wastewater or effluent. The method detects the cyanides that are free (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions. The method does not detect the less toxic strong metal-cyanide complexes, cyanides that are not "amenable to chlorination."

1.2 Total cyanide can be determined for samples that have been distilled as described in Test Methods D2036, Test Method A, Total Cyanides after Distillation. The cyanide complexes are dissociated and absorbed into the sodium hydroxide capture solution, which can be analyzed with this test method; therefore, ligand exchange reagents from 8.12 and 8.13 would not be required when determining total cyanide after distillation.

1.3 This procedure is applicable over a range of approximately 2 µg/L to 400 µg/L (parts per billion) available cyanides. Higher concentrations can be analyzed by dilution or lower injection volume.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in 8.6 and Section 9.

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2036 Test Methods for Cyanides in Water
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6696 Guide for Understanding Cyanide Species
D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129 and Guide D6696.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *available cyanides, n*—Inorganic cyanides that are free (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions.

3.2.1.1 *Discussion*—Available cyanide does not include the less toxic strong metal-cyanide complexes, cyanides that are not "amenable to chlorination" and includes weak acid dissociable or weak and dissociable (WAD) cyanides for use in the implementation of International Cyanide Management Code.

4. Summary of Test Method

4.1 Complex cyanides bound with nickel or mercury are released by ligand displacement by the addition of a ligand displacement agent, when necessary.

4.2 Other weak and dissociable cyanide species do not require ligand displacement.

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

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

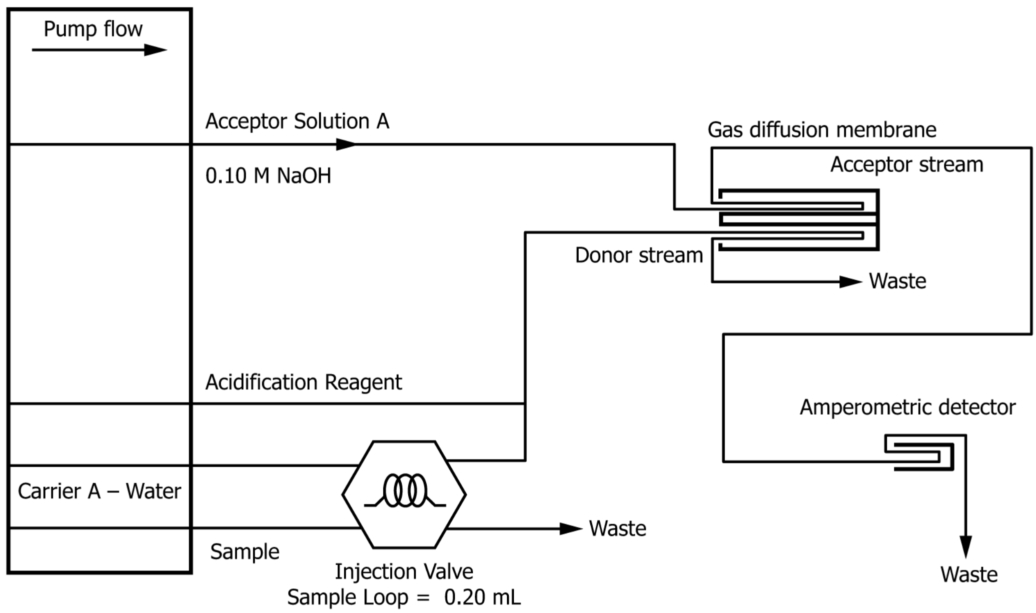

FIG. 1 Flow Injection Analysis Apparatus 1

4.3 The sample is introduced into a flow injection analysis (FIA) system where it is acidified to form hydrogen cyanide (HCN). The hydrogen cyanide gas diffuses through a hydrophobic gas diffusion membrane, from the acidic donor stream into an alkaline acceptor stream.

4.4 The captured cyanide is sent to an amperometric flowcell detector with a silver-working electrode. In the presence of cyanide, silver in the working electrode is oxidized at the applied potential. The anodic current measured is proportional to the concentration of cyanide in the standard or sample injected.

4.5 Calibrations and data are processed with the instrument's data acquisition software.

5. Significance and Use

5.1 Cyanide and hydrogen cyanide are highly toxic. Regulations have been established to require the monitoring of cyanide in industrial and domestic wastes and surface waters.[3]

5.2 This test method is applicable for natural water, saline waters, metallurgical process solutions, and wastewater effluent.

5.3 The method may be used for process control in wastewater treatment facilities.

6. Interferences

6.1 High levels of carbonate can release CO_2 into the acceptor stream and cause an interference with the amperometric detector that result in a slight masking effect (15 % negative bias with 20 ppb cyanide in 1500 ppm carbonate). Refer to 11.2 for sample pretreatment.

6.2 Sulfide above 50 mg/L will diffuse through the gas diffusion membrane and can be detected in the amperometric flowcell. Oxidized products of sulfide can also rapidly convert CN^- to SCN^- at a high pH. Refer to Practice D7365 for sulfide removal procedures.

6.3 Refer to Practice D7365 for further information on mitigating interferences in water samples for the analysis of cyanide.

7. Apparatus

7.1 The instrument should be equipped with a precise sample introduction system, a gas diffusion manifold with hydrophobic membrane, and an amperometric detection system to include a silver working electrode, a Ag/AgCl reference electrode, and a Pt or stainless steel counter electrode. Examples of the apparatus schematics are shown in Figs. 1-3. Example instrument settings are shown in Table 1.[4]

NOTE 1—The instrument settings in Table 1 are only examples. The analyst may modify the settings as long as performance of the method has not been degraded. Contact the instrument manufacturer for recommended instrument parameters.

7.2 An autosampler is recommended but not required to automate sample injections and increase throughput. Autosamplers are usually available as an option from the instrument's manufacturer.

7.3 *Data Acquisition System*—Use the computer hardware and software recommended by the instrument manufacturer to control the apparatus and to collect data from the detector.

[3] 40 CFR Part 136.

[4] OI Analytical CNSolution 3100, FS3100, or Flow Solution IV and Lachat Instruments QuikChem Automated Ion Analyzer using Method 10-204-00-5-A have been found to be suitable for this analysis. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.

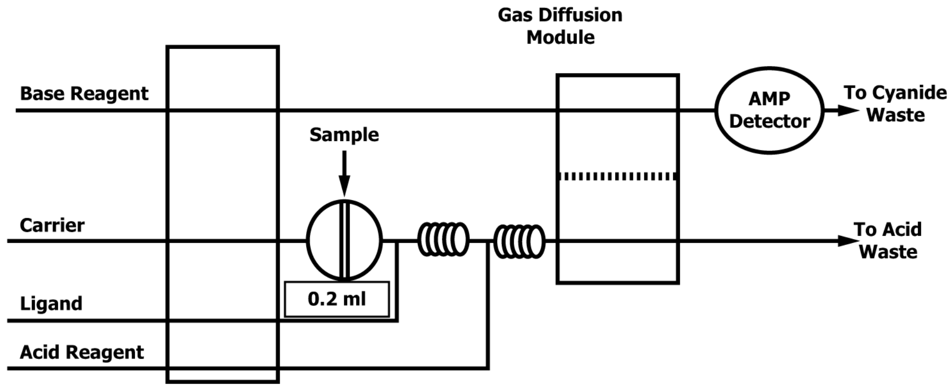

FIG. 2 Flow Injection Apparatus 2 with Automated Ligand Injection

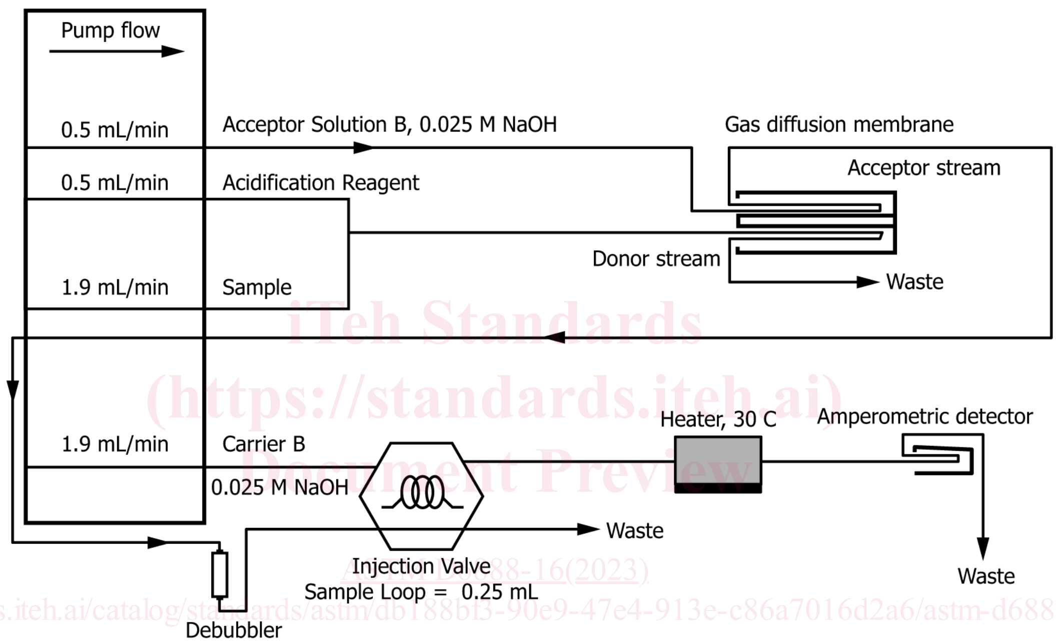

FIG. 3 Flow Injection Analysis Apparatus 3

TABLE 1 Flow Injection Analysis Parameters

FIA Instrument Parameter	Recommended Method Setting
Pump Flow Rates	0.5 to 2 mL/min
Cycle period (total)	90 to 250 s/sample
Sample load period	At least enough time to completely fill the sample loop
Reagent water rinse time between samples	At least 15 s
Peak Evaluation	Peak height or area
Working Potential	0.0 V vs Ag/AgCl

7.4 *Pump Tubing*—Use tubing recommended by instrument manufacturer. Replace pump tubing when worn, or when precision is no longer acceptable.

7.5 *Gas Diffusion Membranes*—A hydrophobic membrane which allows gaseous hydrogen cyanide to diffuse from the donor to the acceptor stream at a sufficient rate to allow detection. The gas diffusion membrane should be replaced when the baseline becomes noisy or every 1 to 2 weeks.[5]

7.6 Use parts and accessories as directed by instrument manufacturer.

8. Reagents and Materials

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 American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that

[5] PALL Life Sciences Part Number M5PU025, OI Analytical Part Number A001520, and Lachat Instruments Part Number 50398 have found to be suitable for this analysis.

[6] *ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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 shall be understood to mean reagent water conforming to Type II grade of Specification D1193.

8.3 *Sodium Hydroxide Solution* (1.00 M)—Dissolve 40 g NaOH in laboratory water and dilute to 1 L.

8.4 *Acceptor Solution A* (0.10 M NaOH)—Dissolve 4.0 g NaOH in laboratory water and dilute to 1 L.

8.5 *Acceptor Solution B, Carrier B* (0.025 M NaOH)—Dissolve 1.0 g NaOH in laboratory water and dilute to 1 L.

8.6 *Stock Cyanide Solution* (1000 µg/mL CN^-)—Dissolve 2.51 g of KCN and 2.0 g of NaOH in 1 L of water. Standardize with silver nitrate solution as described in Test Methods D2036, Section 16.2. Store the solution under refrigeration and check concentration approximately every 6 months and correct if necessary.[7] (**Warning—**Because KCN is highly toxic, avoid contact or inhalation.)

8.7 *Intermediate Cyanide Standards:*

8.7.1 *Intermediate Cyanide Standard 1* (100 µg/mL CN^-)—Pipette 10.0 mL of stock cyanide solution (see 8.6) into a 100 mL volumetric flask containing 1 mL of 1.0 M NaOH (see 8.3). Dilute to volume with laboratory water. Store under refrigeration. The standard should be stable for 6 months.

8.7.2 *Intermediate Cyanide Standard 2* (10 µg/mL CN^-)—Pipette 10.0 mL of Intermediate Cyanide Standard 1 (see 8.7.1) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. Store under refrigeration. The standard should be stable for 6 months.

8.8 *Working Cyanide Calibration Standards*—Prepare fresh weekly as described in 8.8.1 and 8.8.2 ranging in concentration from 2 µg/L to 400 µg/L CN^-.

8.8.1 *Calibration Standards* (20 µg/L, 50 µg/L, 100 µg/L, 200 µg/L, and 400 µg/L CN^-)—Pipette 20 µL, 50 µL, 100 µL, 200 µL, and 400 µL of Intermediate Cyanide Standard 1 (see 8.7.1) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.8.2 *Calibration Standards* (2 µL and 10 µg/L CN^-)—Pipette 20 µL and 100 µL of Intermediate Cyanide Standard 2 (see 8.7.2) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.9 *Cyanide Electrode Stabilization Solution* (2 mg/L as CN^-)—Pipette 200 µL of Stock Cyanide (see 8.6) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. The solution should be stored under refrigeration.

8.10 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of laboratory water. Add glacial acetic acid (approximately 500 mL) to yield a pH of 4.5.

8.11 *Carrier A*—Use water as the carrier.

8.12 *Ligand Exchange Reagent 1* (TEP Solution)—Weigh 0.10 g tetraethylenepentamine (TEP) into a 100 mL volumetric flask. Dilute to volume with laboratory water. The solution should be stored at room temperature.

8.13 *Ligand Exchange Reagent 2* (Dithizone Solution)—Weigh 0.010 g of dithizone into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. Sonicate if necessary until all of the dithizone has dissolved. The solution should be stored at room temperature.

NOTE 2—Commercially prepared or alternative ligand exchange reagents can be used if equivalent results can be demonstrated. Commercial reagents should be used in accordance with manufacturer's instructions.[8]

8.14 *Mixed Ligand Exchange Reagent,* for automated ligand addition as shown in Fig. 2—Transfer 0.125 mL of WAD Reagent A and 0.250 mL of WAD Reagent B8 into a 100 mL volumetric flask containing 50 mL laboratory water. Dilute to volume with laboratory water and mix. The solution should be stored at room temperature

8.15 *Mercury (II) Cyanide Stock Solution*—Weigh 0.4854 g $Hg(CN)_2$ into a 100 mL volumetric flask. Place 1.0 mL of 1.00 M NaOH (see 8.3) in the flask and dilute to volume with laboratory water. $Hg(CN)_2$ as CN^- = 1000 mg/L. The solution must be stored in an amber glass bottle under refrigeration. The standard should be stable for 6 months.

8.16 *Mercury (II) Cyanide Intermediate Solution*—Pipet 10.0 mL of the mercury (II) cyanide stock solution (see 8.15) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory grade water. $Hg(CN)_2$ as CN^- = 100 mg/L. The solution must be stored in an amber glass bottle under refrigeration. The standard should be stable for 6 months.

8.17 *Mercury (II) Cyanide Recovery Solution*—Pipet 100 µL of mercury II cyanide intermediate solution (see 8.16) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water. $Hg(CN)_2$ as CN^- = 100 µg/L. Prepare fresh weekly.

8.18 *Potassium Nickel Cyanide Stock Solution*—Weigh 0.2488 g of $K_2Ni(CN)_4\ H_2O$ in a 100 mL volumetric flask. Place 1.0 mL of 1.00 M NaOH (see 8.3) in the flask and dilute to volume with laboratory water. $K_2Ni(CN)_4$ as CN^- = 1000 mg/L. The solution must be stored in an amber glass bottle under refrigeration. The standard should be stable for 6 months.

8.19 *Potassium Nickel Cyanide Intermediate Solution*—Pipet 10.0 mL of the potassium nickel cyanide stock solution (see 8.18) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory grade water. $K_2Ni(CN)_4$ as CN^- = 100 mg/L. The solution must be stored in an amber glass bottle under refrigeration. The standard should be stable for 6 months.

[7] Commerical Solutions of Stock Cyanide may be substituted.

[8] OI Analytical WAD Reagents A and B, PN A001416 and A001417 have found to be suitable for this analysis.