Designation: D 6888 – 03

An American National Standard

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

This standard is issued under the fixed designation D 6888; 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 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 This procedure is applicable over a range of approximately 2 to 400 µg/L (parts per billion) available cyanide. Higher concentrations can be analyzed by dilution or lower injection volume.

1.3 *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.* Specific hazard statements are given in Note 2 and Section 9.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1129 Terminology Relating to Water[2]
D 1193 Specification for Reagent Water[2]
D 2036 Test Methods for Cyanides in Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water[2]
D 3370 Practices for Sampling Water[2]
D 3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water[2]
D 4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data[2]
D 4375 Terminology for Basic Statistics in Committee D-19 on Water[2]
D 5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis[3]
D 6696 Guide for Understanding Cyanide Species[3]
E 60 Practice for Photometric and Spectrophotometric Methods for Chemical Analysis of Metals[4]
E 275 Practice for Describing and Measuring Performance of Ultraviolet, Visible, and Near Infrared Spectrophotometers[5]
E 1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129 and Guide D 6696.

3.2 *available cyanide*—Inorganic cyanides that are free (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions. Available cyanide does not include the less toxic strong metal-cyanide complexes, cyanides that are not "amenable to chlorination."

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 prior to analysis.

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

4.3 The treated 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 CN^- is captured in the alkaline acceptor stream which then flows into an amperometric flowcell detector with a silver working electrode.

4.5 The cyanide oxidizes the silver electrode causing an amperometric current, which is detected. The current at any time is proportional to the concentration of cyanide flowing past the detector.

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

[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 of Organic Substances in Water.
Current edition approved March 10, 2003. Published May 2003.
[2] *Annual Book of ASTM Standards*, Vol 11.01.
[3] *Annual Book of ASTM Standards*, Vol 11.02.
[4] *Annual Book of ASTM Standards*, Vol 03.05.
[5] *Annual Book of ASTM Standards*, Vol 03.06.

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.[6]

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

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

5.4 The spot test outlined in Test Methods D 2036, Annex A1 can be used to detect cyanide and thiocyanate in water or wastewater, and to approximate its concentration.

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 11.1 for sample pretreatment.

6.2 Sulfide 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 11.3 for sulfide removal.

6.3 Refer to section 6.1 of Test Methods D 2036 for additional information regarding interferences for the analysis of cyanide and Section 11 of Test Methods D 2036 for elimination of interferences.

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 and 2. Example instrument settings are shown in Table 1.[7]

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.

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 pervaporate 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.[8]

7.6 Use parts and accessories as directed by instrument manufacturer.

[6] 40 CFR Part 136.

[7] Both the ALPKEM CN Solution 3000 equipped with an amperometric flowcell, Available from O.I. Analytical, and Lachat Instruments QuikChem Automated Ion Analyzer using Method 10-204-00-5-A have been found to be suitable for this analysis.

[8] Gelmen Sciences Part Number M5PU025, ALPKEM Part Number A0015200, and Lachat Instruments Part Number 50398 have found to be suitable for this analysis.

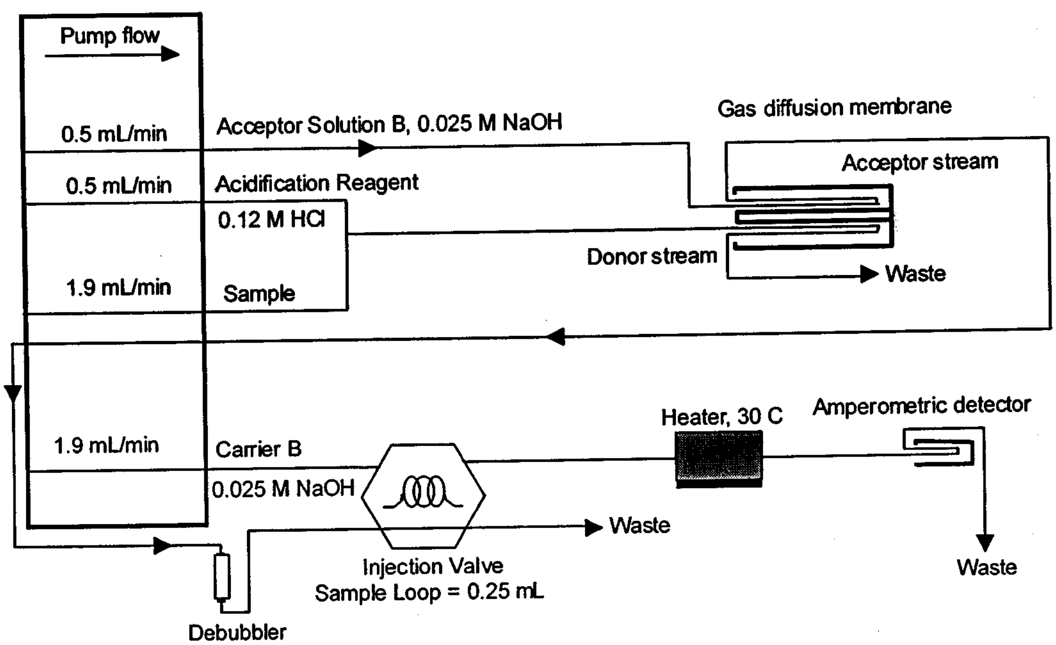

FIG. 1 Flow Injection Analysis Apparatus 1

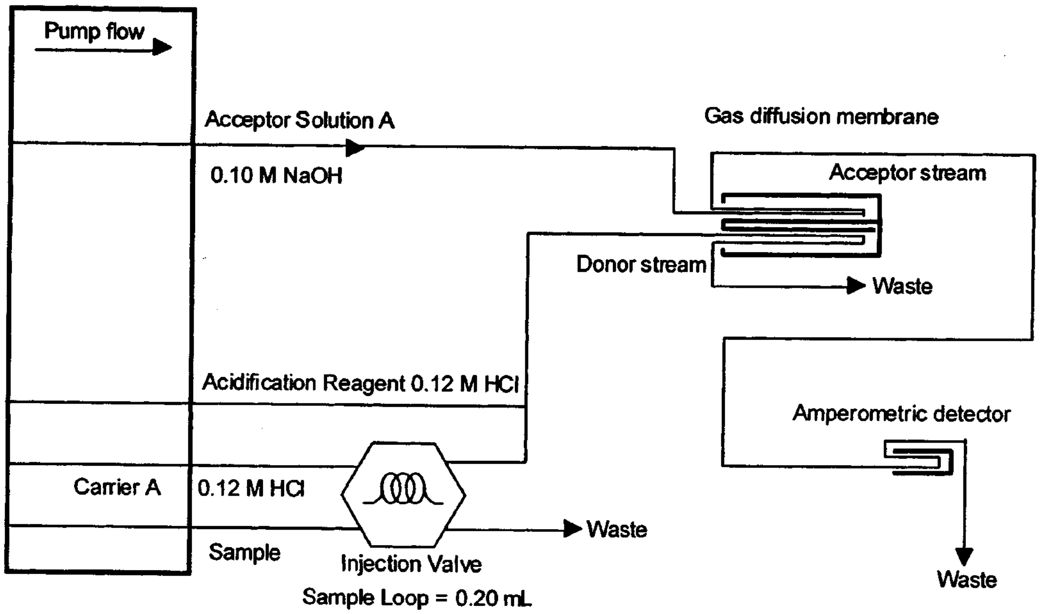

FIG. 2 Flow Injection Analysis Apparatus 2

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

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.[9] 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 shall be understood to mean reagent water conforming to Type II grade of Specification D 1193.

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 D 2036, section 16.2. Store the solution under refrigeration and check concentration approximately every 6 months and correct if necessary.[10]

NOTE 2—**Warning:** Because KCN is highly toxic, avoid contact or inhalation.

8.7 *Intermediate Cyanide Standards*:

8.7.1 *Intermediate 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 at least 2 weeks.

8.7.2 *Intermediate Cyanide Solution 2* (10 µg/mL CN^-)—Pipette 10.0 mL of Intermediate Cyanide Solution 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. The standard should be stable for at least 2 weeks.

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

8.8.1 *Calibration Standards* (20, 50, 100, 200, and 400 µg/L CN^-)—Pipette 20, 50, 100, 200, and 400 µL of Intermediate 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 and 10 µg/L CN^-)—Pipette 20 and 100 µL of Intermediate Cyanide Solution 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 Shocking Solution* (Approximately 5 ppm as CN^-)—Pipette 500 µL of Stock Cyanide (see 8.6) into a 100

[9] *Reagent Chemicals, American Chemical Society Specifications*, Am. Chemical Soc., 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*.

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