



Standard Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection¹

This standard is issued under the fixed designation D 7237; 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 establish the concentration of aquatic “free” cyanide in an aqueous wastewater or effluent. The test conditions of this method are used to measure free cyanide (HCN and CN^-) and cyanide bound in the metal-cyanide complexes that are easily dissociated into free cyanide ions at the pH of the aquatic environment ranging from pH 6 to pH 8. The extent of HCN formation is less dependent on temperature than the pH; however, the temperature can be regulated if deemed necessary to further simulate the actual aquatic environment.

1.2 The aquatic free cyanide method is based on the same instrumentation and technology that is described in standard test method **D 6888**, but employs milder conditions (pH 6-8 buffer versus HCl in the reagent stream), and does not utilize ligand displacement reagents.

1.3 The aquatic free cyanide measured by this procedure should be similar to actual levels of HCN in the original aquatic environment. This in turn may give a reliable index of toxicity to aquatic organisms.

1.4 This procedure is applicable over a range of approximately 2 to 500 $\mu\text{g/L}$ (parts per billion) aquatic free cyanide. Sample dilution may increase cyanide recoveries depending on the cyanide speciation; therefore, it is not recommended to dilute samples. Higher concentrations can be analyzed by increasing the range of calibration standards or with a lower injection volume. In accordance with Guide **E 1763** and Practice **D 6512** the lower scope limit was determined to be 9 $\mu\text{g/L}$ for chlorinated gold leaching barren effluent water.

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 and health practices and determine the applica-*

bility of regulatory limitations prior to use. Specific hazard statements are given in Section 8.6 and Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

- D 1129** Terminology Relating to Water
- D 1193** Specification for Reagent Water
- D 1293** Test Methods for pH of Water
- D 2036** Test Methods for Cyanides in Water
- D 2777** Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D 3370** Practices for Sampling Water from Closed Conduits
- D 3856** Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water
- D 4841** Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
- D 5847** Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- D 6512** Practice for Interlaboratory Quantitation Estimate
- D 6696** Guide for Understanding Cyanide Species
- D 6888** Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
- E 691** Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method
- E 1763** Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods

3. Terminology

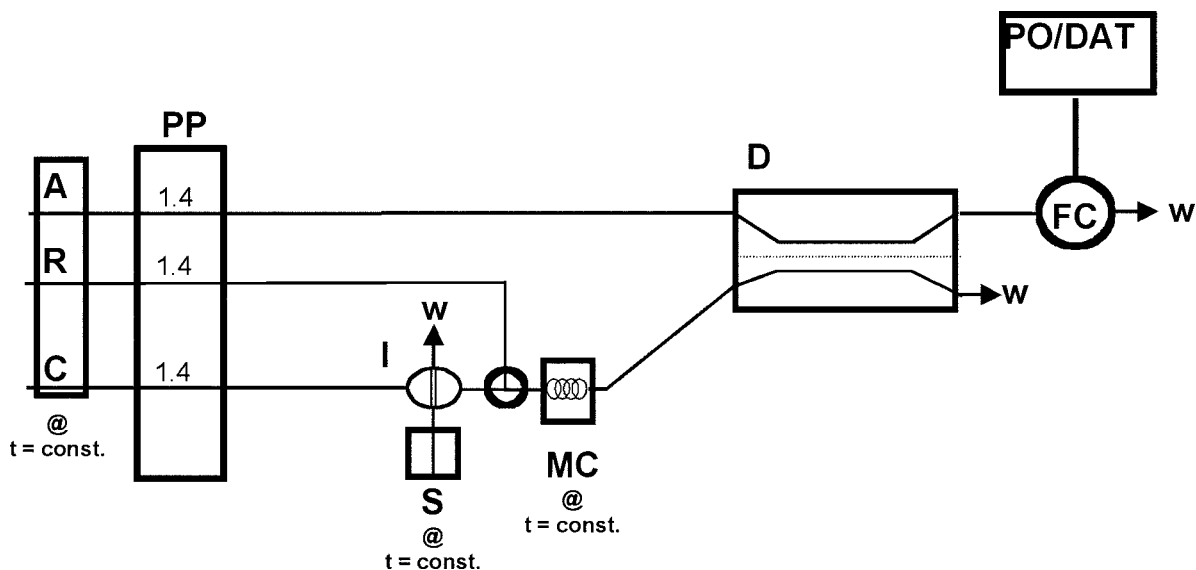
3.1 *Definitions* For definitions of terms used in this test method, refer to Terminology **D 1129** and Guide **D 6696**.

3.1.1 *aquatic free cyanide*—Sum of the free cyanide (HCN and CN^-) and cyanide bound in the metal-cyanide complexes

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.

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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.



C = carrier (water), R = reagent buffer (variable: pH 6-8, 0.2M phosphate buffer), A = acceptor solution (0.1M NaOH), S = sample, P = peristaltic pump (flow rates in mL/min), I = injection valve (200 μ L sample loop), MC = mixing coil (30-60 cm \times 0.5mm i.d.), positioned in optional constant temperature manifold, D = gas-diffusion cell, FC = amperometric flow cell, PO/DAT = potentiostat/data collection device running data acquisition software, W = waste flows.

FIG. 1 Example of flow injection manifold for the determination of aquatic free cyanide.

that are easily dissociated into free cyanide under the test conditions described in this method.

4. Summary of Test Method

4.1 The test is generally performed at room temperature, but temperature of the sample and flow injection reagents can be regulated to match the aquatic environment if necessary.

4.2 The sample is introduced into a carrier solution of the flow injection analysis (FIA) system via an injection valve and confluent downstream with a phosphate buffer solution at pH in the 6-8 range. The released hydrogen cyanide (HCN) gas diffuses through a hydrophobic gas diffusion membrane into an alkaline acceptor stream where the CN^- is captured and 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.

4.3 Calibrations and sample 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 It is useful to determine the aquatic free cyanide to establish an index of toxicity when a wastewater is introduced to the pH and temperature of the natural environment.

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

6. Interferences

6.1 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 11.2 for sulfide removal.

6.2 Refer to section 6.1 of Test Method D 6888 and Test Method D 2036 for elimination of cyanide 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. An example of the apparatus schematic is shown in Fig. 1. Example instrument settings are shown in Table 1.

NOTE 1—The instrument and settings in Fig. 1 and Table 1 are shown as examples. The analyst may modify these 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. If the sample is to be analyzed at a constant temperature other than the temperature of the room, manual injections may be required unless the autosampler is equipped to maintain constant temperature.

7.3 If aquatic free cyanide at a temperature other than room temperature is required, a constant temperature bath capable of maintaining the temperature of the aquatic environment within $\pm 0.5^\circ C$ should be used to regulate the temperature of the flow injection reagents and samples.

7.4 *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.

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

³ 40 CFR Part 136.

TABLE 1 Flow Injection Analysis Parameters

FIA Instrument Parameter	Recommended Method Setting
Pump Flow Rates	0.5 to 2.0 mL/min
Cycle period (total)	Approximately 120 seconds
Sample load period	At least enough time to completely fill the sample loop prior to injection
Injection valve rinse time between samples	At least enough time to rinse the sample loop
Peak Evaluation	Peak height or area
Working Potential	0.0 V vs Ag/AgCl

7.6 *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.

7.7 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.⁴ 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 that meets the purity specifications of Type I or Type II water, presented in **D 1193**.

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

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

8.5 *Carrier*—Water, as described in section 8.2.

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.⁵ (**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 500 µg/L CN⁻.

8.8.1 *Calibration Standards (20, 50, 100, 200, and 500 µg/L CN⁻)*—Pipette 20, 50, 100, 200, and 500 µL of Intermediate Standard 1 (see 8.7.1) into separate 100 mL volumetric flasks containing 1.0 mL of 0.10 M NaOH (see 8.4). Dilute to volume with laboratory water.

8.8.2 *Calibration Standards (2, 5, and 10 µg/L CN⁻)*—Pipette 20, 50, and 100 µL of Intermediate Cyanide Solution 2 (see 8.7.2) into separate 100 mL volumetric flasks containing 1.0 mL of 0.10 M NaOH (see 8.4). Dilute to volume with laboratory water.

8.9 *Cyanide Electrode Stabilization Solution (Approximately 5 ppm as CN⁻)*—Pipette 500 µL of Stock Cyanide (see 8.6) into a 100 mL volumetric flask containing 1.0 mL of 0.10M M NaOH (see 8.4). Dilute to volume with laboratory water. The solution should be stored under refrigeration.

8.10 *Acetate Buffer*—Dissolve 410 g of sodium acetate trihydrate (NaC₂H₃O₂·3H₂O) in 500 mL of laboratory water. Add glacial acetic acid (approximately 500 mL) to yield a pH of 4.5.

8.11 *Buffer Solution A, 2M Sodium phosphate monobasic solution*—Weigh 276 g sodium phosphate monobasic monohydrate (NaH₂PO₄·H₂O) in a 1 L volumetric flask. Dissolve and dilute to volume with water.

8.12 *Buffer Solution B, 2M Sodium phosphate dibasic solution*—Weigh 284 g sodium phosphate dibasic, anhydrous (Na₂HPO₄) in a 1 L volumetric flask. Dissolve and dilute to volume with water. If necessary, warm to approximately 40°C on a hot plate and stir to completely dissolve the sodium phosphate dibasic into the water. Allow the solution to cool prior to use.

8.13 *1M Phosphate Buffer pH 7.0 Stock Solution*—Add 97.5 mL Buffer Solution A and 152.5 mL Buffer Solution B to a 500 mL volumetric flask. Dilute to volume with water.

8.14 *0.2 M Phosphate Buffer pH 7.0*—In a 1 L volumetric flask, add 200 mL 1M Phosphate Buffer Solution pH 7.0 and dilute to volume with water. The pH should be pH 7.0 ± 0.1. Verify the pH as described in **D 1293** (Test Method A) and adjust if necessary with dilute sodium hydroxide or sulfuric acid. This buffer solution is to be used in the FIA system when aquatic free cyanide is to be determined at pH 7.0.

8.15 *1M Phosphate Buffer pH 6.0 Stock Solution*—Add 219.25 mL Buffer Solution A and 30.75 mL of Buffer Solution B to a 500 mL volumetric flask. Dilute to volume with water.

8.16 *0.2 M Phosphate Buffer pH 6.0*—In a 1 L volumetric flask, add 200 mL 1M Phosphate Buffer Solution pH 6.0 and dilute to volume with water. The pH should be pH 6.0 ± 0.1. Verify the pH as described in **D 1293** (Test Method A) and adjust if necessary with dilute sodium hydroxide or sulfuric

⁴ *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*.

⁵ Commercial Solutions of Stock Cyanide may be substituted.