



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

This standard is issued under the fixed designation D7237; 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 free cyanide in an aqueous wastewater, effluent and in-stream free cyanide concentrations after mixing treated water with receiving water. The test conditions of this test 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 6. Free cyanide is determined at pH 6 at room temperature. The aquatic free cyanide can be determined by matching the pH to the water in the receiving environment in the range of pH 6 to 8. The extent of HCN formation is less dependent on temperature than the pH; however, the temperature can be regulated if deemed necessary for aquatic free cyanide to further simulate the actual aquatic environment.

1.2 The free cyanide test method is based on the same instrumentation and technology that is described in Test Method [D6888](#), but employs milder conditions (pH 6–8 buffer versus HCl or H_2SO_4 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 5 to 500 $\mu\text{g/L}$ (parts per billion) 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 [E1763](#) and Practice [D6512](#) the lower scope limit was determined to be 9 $\mu\text{g/L}$ for chlorinated gold leaching barren effluent water and the $\text{IQE}_{10\%}$

is 12 $\mu\text{g/L}$ in the gold processing detoxified reverse osmosis permeate waste water sample matrix.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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.* Specific hazard statements are given in [8.6](#) and Section [9](#).

2. Referenced Documents

2.1 ASTM Standards:²

- [D1129 Terminology Relating to Water](#)
- [D1193 Specification for Reagent Water](#)
- [D1293 Test Methods for pH of Water](#)
- [D2036 Test Methods for Cyanides in Water](#)
- [D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water](#)
- [D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water](#)
- [D4841 Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents](#)
- [D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis](#)
- [D6512 Practice for Interlaboratory Quantitation Estimate](#)
- [D6696 Guide for Understanding Cyanide Species](#)
- [D6888 Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis \(FIA\) Utilizing Gas Diffusion Separation and Amperometric Detection](#)
- [D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide](#)
- [D7728 Guide for Selection of ASTM Analytical Methods for Implementation of International Cyanide Management Code Guidance](#)

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.

*A Summary of Changes section appears at the end of this standard

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E1601 Practice for Conducting an Interlaboratory Study to Evaluate the Performance of an Analytical Method

E1763 Guide for Interpretation and Use of Results from Interlaboratory Testing of Chemical Analysis Methods (Withdrawn 2015)³

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology **D1129** and Guide **D6696**.

3.1.1 *aquatic free cyanide, n*—free cyanide measured when the buffer or temperature is adjusted to mimic the receiving-water environment.

3.1.2 *free cyanide, n*—sum of the free cyanide (HCN and CN⁻) and cyanide bound in the metal-cyanide complexes that are easily dissociated into free cyanide under the test conditions described in this test method at pH 6 and room temperature.

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 to measure aquatic free cyanide.

4.2 The sample is introduced into a carrier solution of the flow injection analysis (FIA) system via an injection valve and confluence downstream with a phosphate buffer solution at pH 6 to measure free cyanide or in the range of pH 6 to 8 to measure aquatic free cyanide. 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.⁴

5.2 It is useful to determine the aquatic free cyanide to establish an index of toxicity when a wastewater is introduced into the natural environment at a given pH and temperature.

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

5.4 Free cyanide measured using this test method is applicable for implementation of the International Cyanide Code Guidance in accordance with Guide **D7728**.

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 **11.3** for sulfide removal.

6.2 Refer to 6.1 of Test Method **D6888** and Test Methods **D2036** for elimination of cyanide interferences.

6.3 Residual flotation reagents have been shown to interfere,⁵ which is indicated by failure of the amperometric signal to return to baseline compared to the standards. This effect is attributed to the formation of volatile carbon disulfide. If this interference is encountered, verify by comparing with analysis using Test Method **D6888** including bismuth nitrate in the acidification reagent on a solution without sodium hydroxide preservation, which should provide confirmation due to lower results.

7. Apparatus

7.1 The instrument must 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 $\pm 0.5^{\circ}\text{C}$ 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.

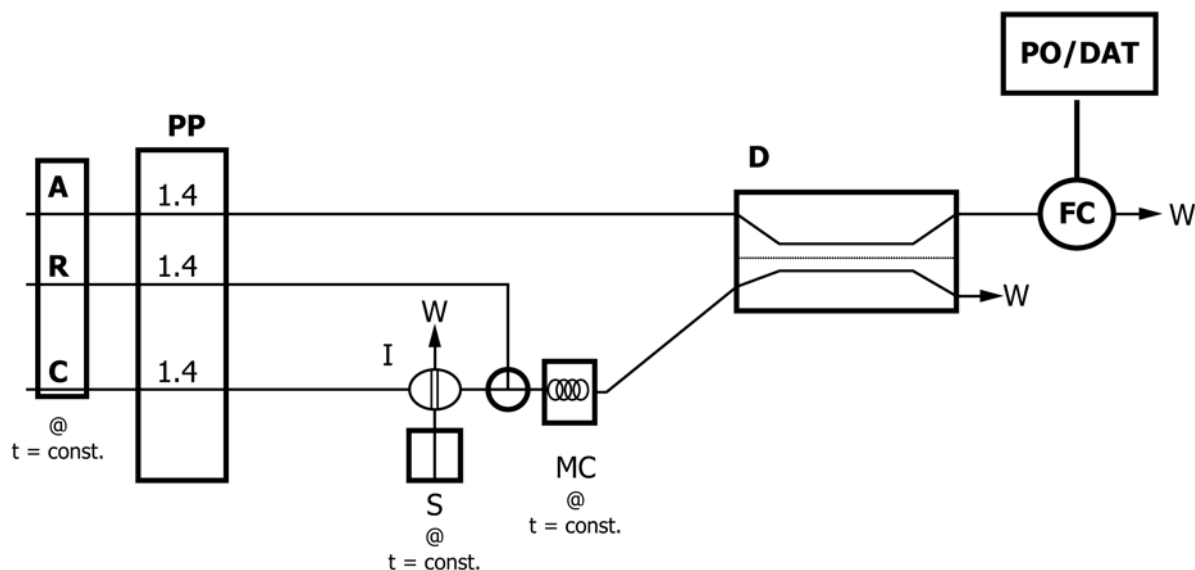
7.5 *Pump Tubing*—Use tubing recommended by instrument manufacturer. Replace pump tubing when worn, or when precision is no longer acceptable.

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.

³ The last approved version of this historical standard is referenced on www.astm.org.

⁴ 40 CFR Part 136.

⁵ Solujic, L., and Milosavljevic, E., *Flotation Reagents Testing and Analyses of Cyanide Spiked Samples*, Report to Newmont Mining Corporation, July 30, 2011.



C = carrier (water), R = reagent buffer (variable: pH 6 for free cyanide and pH 6-8 for aquatic free cyanide, 0.2 M phosphate buffer), A = acceptor solution (0.1 M 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 0.5 mm 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

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

7.7 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.⁶ 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 Specification D1193.

⁶ *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*.

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

NOTE 2—Acceptor solution concentration of 0.025 M NaOH has also been found to be acceptable.

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

NOTE 3—Carrier solution containing 0.025 M NaOH has also been found to be acceptable.

8.6 *Stock Cyanide Solution (1000 μ g/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, 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 Standard 1 (100 μ g/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 μ g/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 μ g/L CN⁻.

⁷ Commercial Solutions of Stock Cyanide may be substituted.