Designation: D7237 – 15

StandardTest Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection[1]

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 µg/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 µg/L for chlorinated gold leaching barren effluent water and the $IQE_{10\ \%}$ is 12 µg/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 Method 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.

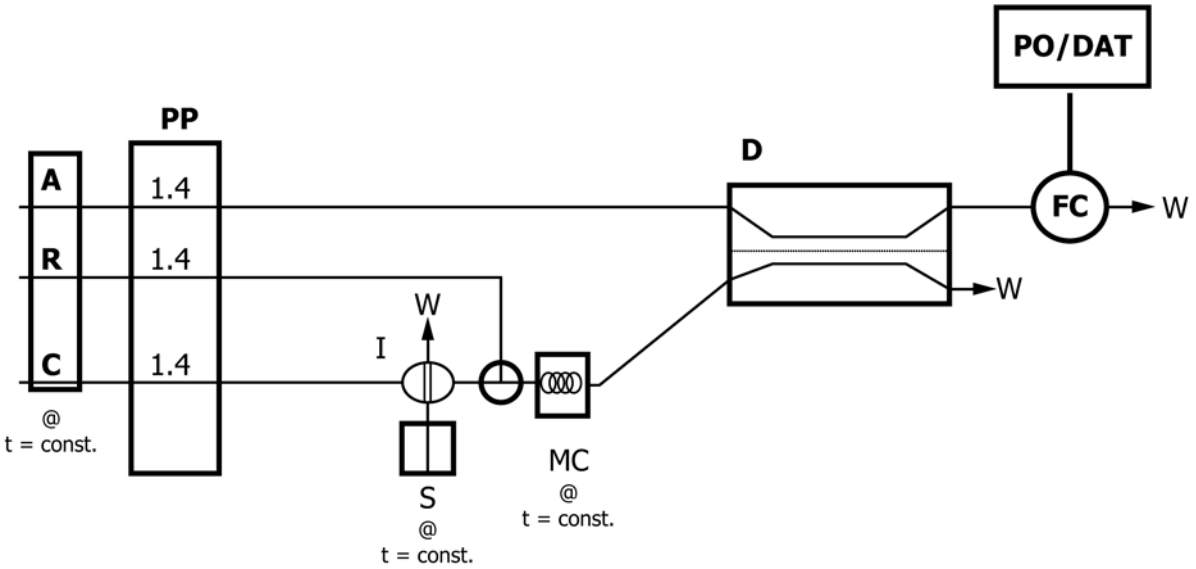
7.3 If aquatic free cyanide at a temperature other than room temperature is required, a constant temperature bath capable of maintaining the temperature of the aquatic environment within ±0.5°C should be used to regulate the temperature of the flow injection reagents and samples.

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 µL sample loop), MC = mixing cool (30–60 cm × 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 D1193.

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 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, 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 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^-.

[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*.

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

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 ($NaC_2H_3O_2 \cdot 3H_2O$) in 500 mL of laboratory water. Add glacial acetic acid (approximately 500 mL) to yield a pH of 4.5.

8.11 *Buffer Solution A, 2M Sodium phosphate monobasic solution*—Weigh 276 g sodium phosphate monobasic monohydrate ($NaH_2PO_4 \cdot H_2O$) in a 1 L volumetric flask. Dissolve and dilute to volume with water.

8.12 *Buffer Solution B, 2 M Sodium phosphate dibasic solution*—Weigh 284 g sodium phosphate dibasic, anhydrous (Na_2HPO_4) 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.

8.12.1 Alternatively, prepare a 1 M solution by dissolving 142 g sodium phosphate dibasic, anhydrous in 1 L.

8.13 *1 M 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.

8.13.1 Alternatively, substitute 305 mL of 1 M sodium phosphate dibasic for the 152.5 mL of Buffer Solution B.

8.14 *0.2 M Phosphate Buffer pH 7.0*—In a 1 L volumetric flask, add 200 mL 1 M 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 D1293 (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 *1 M 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.

8.15.1 Alternatively, substitute 61.5 mL of 1 M sodium phosphate dibasic for the 30.75 mL of Buffer Solution B.

8.16 *0.2 M Phosphate Buffer pH 6.0*—In a 1-L volumetric flask, add 200 mL 1 M 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 D1293 (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 free cyanide or aquatic free cyanide is to be determined at pH 6.0 or if the pH of the aquatic environment has not been specified.

8.17 *1 M Phosphate Buffer pH 8.0 Stock Solution*—Add 10.0 mL Buffer Solution A and 240 mL Buffer Solution B to a 500-mL volumetric flask. Dilute to volume with water.

8.18 *0.2 M Phosphate Buffer pH 8.0*—In a 1-L volumetric flask, add 200 mL 1 M Phosphate Buffer Solution pH 8.0 and dilute to volume with water. The pH should be pH=8.0 ± 0.1. Verify the pH as described in D1293 (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 8.0.

8.19 *Ag/AgCl Reference Electrode Filling Solution*—Fill the reference electrode as recommended by the instrument manufacturer.

9. Hazards

9.1 **Warning**—Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). All manipulations must be done in the hood so that any HCN gas that might escape is safely vented.

9.2 **Warning**—Many of the reagents used in these test methods are highly toxic. These reagents and their solutions must be disposed of properly.

9.3 All reagents and standards should be prepared in volumes consistent with laboratory use to minimize the generation of waste.

10. Sample and Sample Preservation

10.1 Collect the sample in accordance with latest version of Practice D7365. This practice is applicable for the collection and preservation of water samples for the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated. Usually 100 mL sample volume is sufficient. Samples must be collected and stored in dark (amber or low actinic) containers to minimize reactions of ultra violet light.

10.2 The sample must be stabilized at time of collection with the addition of sodium hydroxide. Add 1 mL of 0.1 M NaOH to 100 mL of the sample or until the sample is pH 11.

10.3 See Section 11 if oxidizing agents or sulfide are suspected to be present in the sample.

10.4 Samples must be stored in dark bottles that minimize exposure to ultraviolet radiation and refrigerated.

NOTE 4—Practice D7365 recommends refrigeration by storing the sample between its freezing point and 6°C.

10.5 Synthetic samples have been shown to be stable for at least 14 days and up to 30 days, but in actual samples the cyanide concentrations may decrease significantly prior to this holding time if there are undetectable traces of chlorine, reduced sulfur species, or hydrogen peroxide present. Analyze the sample as soon as possible to avoid degradation. Holding times can be estimated in accordance with Practice D4841.

11. Elimination of Interferences

11.1 Practice D7365 specifies mitigation of interference procedures for testing water samples for cyanide.

11.2 *Oxidizing Agent*—Test for the presence of oxidizing agents. Add a drop of the sample to acidified KI starch test paper (acidify KI starch paper with acetate buffer, see 8.10) as soon as the sample is collected; a blue color indicates the need for treatment. If oxidizing agents are present, add 0.1 g/L sodium arsenite to the sample to avoid degradation of cyanide.

11.3 *Sulfide*—Test for sulfide by placing a drop of sample on lead acetate paper previously moistened with acetate buffer solution (see 8.10). If the paper turns black, sulfide is present. Add lead acetate, or if the sulfide concentration is too high, add powdered lead carbonate to avoid significantly reducing the pH. Repeat this test until a drop of treated sample no longer darkens the acidified lead acetate test paper. The supernatant containing cyanide must be filtered immediately to avoid the rapid loss of cyanide due to the formation of thiocyanate.

NOTE 5—Lead acetate test strips may not be sensitive enough to detect sulfide concentrations below approximately 50 mg/L; therefore, treatment may be performed on samples where sulfide is suspected. Interference can be confirmed by analyzing the sample with and without treatment. If the measured cyanide in the untreated sample is significantly higher, sulfide is likely present and treatment described in 11.3 should be performed to remove sulfide.

12. Calibration and Standardization

12.1 Turn on the power to the apparatus and the autosampler (if equipped). Start the data acquisition system.

12.2 Clamp the pump tube platens in place and start pumping reagents in the flow injection system. Allow the system to warm up at least 15 min or until a stable baseline is achieved. Take care not to over-tighten the pump tube platens as this greatly reduces the lifetime of the tubing.

12.3 If recommended by the instrument manufacturer, aspirate the Cyanide Stabilization Solution (5 ppm CN^-) from 8.9. After at least 30 s, inject the stabilization solution into the apparatus and record the amperometric response (pA value) after the cycle period has completed. Repeat this procedure until the peak responses are less than 2 % RSD. This process will ensure that the electrode system has stabilized.

12.4 After the electrode system has stabilized, aspirate the highest working standard (see 8.8) into the flow injection apparatus. Follow the instrument manufacturer's instructions to store the retention time window for cyanide using the data acquisition software.

12.5 Select the buffer to be used for instrumental analysis of the sample, which is pH 6 for free cyanide or the closest pH to that of the receiving water for the sample for aquatic free cyanide.

12.6 Inject each working standard and a reagent blank into the apparatus and record the amperometric response with the data acquisition system. Plot the response versus the cyanide concentration with a straight line or a quadratic fit curve depending on the instrument and data acquisition system employed. If the calibration model is polynomial, it may be no more than third order. A second order polynomial is recommended.

NOTE 6—Some regulatory agencies such as the USEPA may not allow use of a third or higher order polynomial for calibration.

12.7 Prepare a new calibration curve at least once daily.

13. Procedure

13.1 If samples were stored under refrigeration, allow the samples to stand at room temperature or place the aquatic free cyanide samples in a constant temperature bath (7.3) until a constant temperature is achieved. Record the temperature to the nearest 0.1°C.

13.2 Inject each sample into the flow injection apparatus, and inspect for irregular peak shapes, disturbances, or detector overloads.

14. Data Analysis and Calculations

14.1 Report the free cyanide result at pH 6. If aquatic free cyanide was determined, report the aquatic free cyanide result in µg/L at the pH of the buffer solution along with the temperature of samples and reagents. Multiply the cyanide result by any dilution factor and round the test result to three significant figures.

Examples:

$$\text{Free Cyanide} = 15.2\ \mu g/L\ CN^- \quad (1)$$

$$\text{Aquatic Free Cyanide} = 15.2\ \mu g/L\ CN^-\ ,\text{pH } 6,25.0°C \quad (2)$$

14.2 Some instruments are capable of performing multiple injections in which the mean result for each sample can be reported. In this case, the mean result should be reported and denoted as such.

15. Precision and Bias[8]

15.1 This test method is based on Test Method D6888 and is expected to have similar performance.

15.2 This test method was evaluated and validated in a single laboratory with synthetic samples, treated gold leaching effluent, and receiving water samples[9]. Portions of the data from this study are shown in Tables 2-5.

15.3 Precision and bias were determined as described in Practice D2777. The samples were evaluated at pH 6 at room temperature with Standard Material 990-011, which is a synthetic precious metals processing wastewater.[10] The sample matrix is described in Table 6. Based on the results of 8 operators in 8 laboratories, the overall and single operator precision and method bias data are shown in Table 7. The synthetic wastewater used in this study contains specific analytes that challenge this test method; however, the results of the collaborative study may not be typical of results for all matrices.

[8] Supporting data are being filed at ASTM International.

[9] Solujic, L., and Milosavljevic, E., "Flow Injection Based Method for Determination of Aquatic Free Cyanide," prepared for Newmont Mining Corporation, Charles Bucknam, 10101 East Dry Creek Road, Englewood, CO 80513, July 18, 2003.

[10] Reference Material SM-990-011 is available from High Purity Standards, Charleston, SC.

TABLE 2 Species and Concentration Dependent Cyanide Recoveries Obtained Using a pH 7 Buffer

	0.500 ppm CN^- level		0.250 ppm CN^- level		0.050 ppm CN^- level	
SPECIES[A]	CN^- found (ppm)	% recovery	CN^- found (ppm)	% recovery	CN^- found (ppm)	% recovery
$[Zn(CN)_4]^{2-}$	0.517 (0.59)	103.4	0.241 (0.24)	96.4	0.047 (1.2)	94.0
$[Cd(CN)_4]^{2-}$	0518 (0.62)	103.6	0.245 (0.12)	98.0	0.050 (2.3)	100.0
$[Hg(CN)_4]^{2-}$	0.267 (2.7)	53.4	0.124 (2.3)	49.6	0.025 (0.29)	50.0
$[Cu(CN)_4]^{3-}$	0.289 (2.9)	57.8	0.135 (0.74)	54.0	0.032 (0.36)	64.0
$[Ag(CN)_2]^-$	0.049 (2.0)	9.8	0.036 (1.6)	14.4	0.013 (0.77)	26.0
$Hg(CN)_2$	0.004 (8.3)	0.8	0.003 (5.8)	1.2	0.002 (1.4)	4.0
$[Ni(CN)_4]^{2-}$	0.007 (3.1)	1.4	0.007 (2.1)	2.8	0.004 (4.3)	8.0
$[Au(CN)_2]^-$	N/D[B]	0.0	N/D	0.0	N/D	0.0
$[Fe(CN)_6]^{4-}$	0.002 (5.1)	0.4	N/D	0.0	N/D	0.0
$[Fe(CN)_6]^{3-}$	0.005 (2.1)	1.0	0.004 (12.5)	1.6	0.002 (6.9)	4.0

[A] RSDs (%) (n = 3) are given in parentheses.
[B] N/D non detect.

TABLE 3 The Effect of the Reagent Stream pH on the Species Dependent Cyanide Recoveries from Various Metal-Cyano Complexes at 0.250 ppm (µg/mL) CN^- Level

	0.250 ppm CN^- level					
	pH 6.0		pH 7.0		pH 8.0	
SPECIES[A]	CN^- found (ppm)	% recovery	CN^- found (ppm)	% recovery	CN^- found (ppm)	% recovery
$[Zn(CN)_4]^{2-}$	0.253 (0.54)	101.2	0.251 (0.73)	100.4	0.253 (1.6)	101.2
$[Cd(CN)_4]^{2-}$	0.256 (1.2)	102.4	0.245 (0.62)	98.0	0.244 (0.24)	97.6
$[Hg(CN)_4]^{2-}$	0.125 (2.0)	50.0	0.127 (1.2)	50.8	0.124 (0.81)	49.6
$[Cu(CN)_4]^{3-}$	0.150 (1.2)	60.0	0.137 (0.42)	54.8	0122 (0.37)	48.8
$[Ag(CN)_2]^-$	0.058 (1.0)	23.2	0.035 (1.3)	14.0	0.023 (2.5)	9.2

[A] RSDs (%) (n=3) are given in parentheses.

TABLE 4 The Effect of Temperature (t) on the Species Dependent Cyanide Recoveries from Various Metal-Cyano Complexes at 0.250 ppm (µg/mL) CN^- Level

	0.250 ppm CN^- level[A]			
	t = 10 ± 0.5°C		t = 30 ± 0.5°C	
SPECIES	CN^- found (ppm)	% recovery	CN^- found (ppm)	% recovery
$[Zn(CN)_4]^{2-}$	0.236 (0.42)	94.4	0.236 (0.24)	94.4
$[Cd(CN)_4]^{2-}$	0.240 (2.7)	96.0	0.243 (0.41)	97.2
$[Hg(CN)_4]^{2-}$	0.121 (1.6)	48.4	0.125 (0.80)	50.0
$[Cu(CN)_4]^{3-}$	0.146 (1.9)	58.4	0.145 (0.75)	58.0
$[Ag(CN)_2]^-$	0.019 (5.2)	7.60	0.037 (1.5)	14.8

[A] RSDs (%) (n=3) are given in parentheses.

TABLE 5 Spike Recoveries in a Precious Metals Leaching Process Sample (R: pH 6 buffer); All Concentrations are in ppm (µg/mL) CN^-

		CN^- Found in the Spiked Sample[A]				
Spike Concentration	Spiking Species	Rep. 1	Rep. 2	Mean	RPD[B] (%)	Spike Recovery (%)
0.050 CN^-	NaCN	0.048 (0.44)	0.048 (0.32)	0.048	0.00	96.0
0.050 CN^-	$[Cu(CN)_4]^{3-}$	0.041 (0.15)	0.041 (1.6)	0.041	0.00	82.0
0.500 CN^-	NaCN	0.498 (1.0)	0.499 (0.20)	0.4985	0.20	99.7
0.500 CN^-	$[Zn(CN)_4]^{2-}$	0.500 (2.9)	0.479 (2.3)	0.4895	4.29	97.9
0.500 CN^-	$[Cu(CN)_4]^{3-}$	0.313 (0.96)	0.309 (0.64)	0.311	1.29	62.2

[A] RSDs (%) (n=3) are given in parentheses.
[B] Relative Percent Difference.

15.4 Two additional samples were tested during the interlaboratory study to evaluate precision: fortified biologically treated wastewater and chlorinated gold leaching barren effluent. Each participating laboratory analyzed both of the samples in triplicate. The precision data, calculated as described in practice E691, are reported in Tables 8 and 9. The chlorinated sample was not stable throughout the duration of the interlaboratory study; therefore, overall precision could not be determined for this particular sample.

15.5 An additional interlaboratory test was conducted to establish the interlaboratory quantitation estimate to determine if quantitative results could be obtained at 5 µg CN^-/L, the guideline established by the Canadian Council of Ministers of the Environment for fresh water receiving waters. A semi-geometrical design was used in accordance with Practices D2777 – 09 and D6512 – 07. The matrix tested was for the gold ore processing detoxified reverse osmosis permeate waste water summarized in Table 10. Instruments were calibrated in the range of 0–100 µg/L CN^- in an attempt to improve the lower quantitation limit of the test method in eight laboratories, one laboratory provided two independent sets of results. Results are summarized in Table 11 for the precision and Table