Designation: D7284 – 13 (Reapproved 2017)

Standard Test Method for
Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection[1]

This standard is issued under the fixed designation D7284; 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 total cyanide in an aqueous wastewater or effluent. This test method detects the cyanides that are free (HCN and CN^-) and strong-metal-cyanide complexes that dissociate and release free cyanide when refluxed under strongly acidic conditions.

1.2 This test method may not be applicable to process solutions from precious metals mining operations.

1.3 This procedure is applicable over a range of approximately 2 to 500 µg/L (parts per billion) total cyanide. Higher concentrations can be measured with sample dilution or lower injection volume.

1.4 The determinative step of this test method utilizes flow injection with amperometric detection based on Test Method D6888. Prior to analysis, samples must be distilled with a micro-distillation apparatus described in this test method or with a suitable cyanide distillation apparatus specified in Test Methods D2036.

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.

1.7 *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
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
D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
D6696 Guide for Understanding Cyanide Species
D6888 Test Method for Available Cyanides 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
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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 *total cyanide, n*—total cyanide is an analytically defined term that refers to the sum total of all of the inorganic chemical forms of cyanide that dissociate and release free cyanide when refluxed under strongly acidic conditions.

3.2.1.1 *Discussion*—Total cyanide is determined analytically through strong acid distillation or UV radiation followed by analysis of liberated free cyanide on aqueous samples preserved with NaOH (pH~12). In water, total cyanide includes the following dissolved species: free cyanide, weak acid dissociable metal cyanide complexes and strong metal cyanide complexes. Also, some of the strong metal cyanide complexes,

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[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.

such as those of gold, cobalt and platinum, might not be fully recovered during the total cyanide analytical procedure. Additionally, total cyanide may also include some organic forms of cyanide such as nitriles that release free cyanide under the conditions of the analysis.

4. Summary of Test Method

4.1 The samples are distilled with a strong acid in the presence of magnesium chloride catalyst and captured in sodium hydroxide absorber solution.

4.2 The absorber solution 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.

4.3 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.

4.4 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 waters, industrial wastewaters and effluents.

6. Interferences

6.1 Improper sample collection or pretreatment can result in significant positive or negative bias, therefore it is imperative that samples be collected and mitigated for interferences as described in Practice D7365.

6.1.1 Sulfide captured in the absorber solution above 50-mg/L S^{2-} will diffuse through the gas diffusion membrane during flow injection analysis and can be detected in the amperometric flowcell as a positive response. Refer to Section 11.2 for sulfide abatement.

6.1.2 Thiocyanate in the presence of oxidants (for example, nitrates, hydrogen peroxide, chlorine or chloramine, Caro's acid), can decompose to form cyanide during the distillation resulting in positive interference regardless of the determinative step (amperometry, colorimetry, etc.). During acidic distillation, decomposition of thiocyanate in the absence of oxidants produces elemental sulfur, sulfur(IV) oxide, as well as carbonyl sulfide which eventually leads to the formation of sulfite ion (SO_3^{2-}) in the NaOH absorbing solution. The sulfite ion slowly oxidizes cyanide to cyanate resulting in a negative interference. Therefore, samples that are known to contain significant amounts of thiocyanate may need to be analyzed with a test method that does not require distillation, for example, available cyanide by Test Method D6888.

6.1.2.1 During the validation study, synthetic samples containing up to 15 mg/L SCN^- and 25 mg/L NO_3 as N yielded less than 0.5 % of the SCN^- to be measurable CN^-. For example, a solution that did not contain any known amount of cyanide, but did contain 15-mg/L SCN^- and 25 mg/L NO_3 as N, was measured as 53.1 µg/L CN^-.

7. Apparatus and Instrumentation

7.1 The instrument should be equipped with a precise sample introduction system, a gas diffusion manifold with

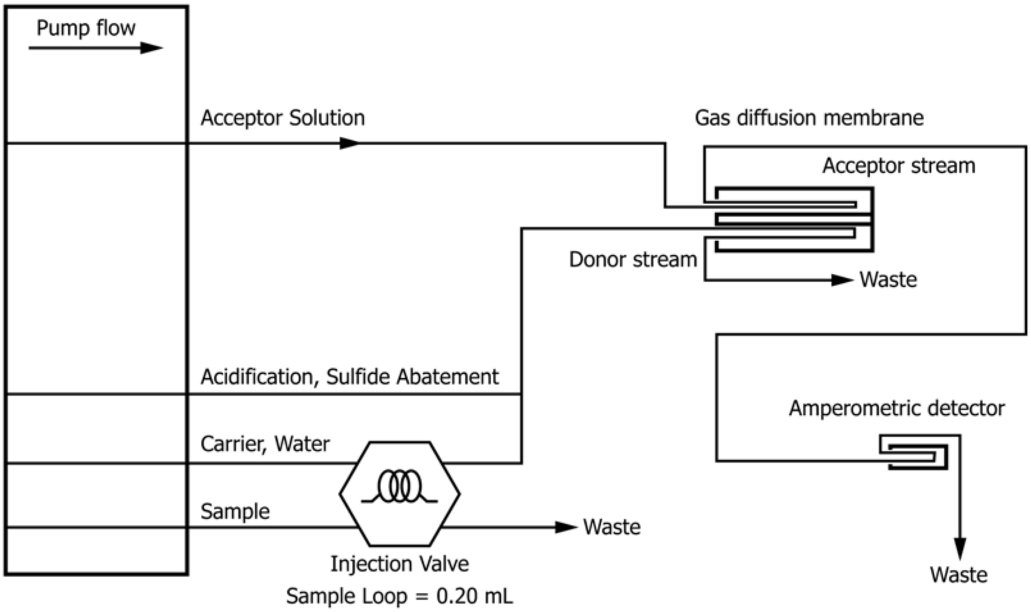

FIG. 1 Flow Injection Analysis Apparatus

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[3] 40 CFR Part 136.

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. The apparatus schematic is shown in Fig. 1, and 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.

7.1.1 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.

7.1.2 *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.

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

7.1.4 *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]

7.1.5 Use parts and accessories as directed by instrument manufacturer.

7.2 *Distillation Apparatus*—The Micro-Distillation System described below was utilized during the laboratory study to demonstrate precision and bias for this test method. A larger distillation apparatus such as the MIDI distillation described in Section 7 of Test Methods D2036 can also be used to prepare samples prior to flow injection analysis, but the user is responsible to determine the precision and bias.

7.2.1 Micro-Distillation Apparatus consisting of a distillation sample tube, hydrophobic membrane, and collector tube containing 1.5 mL of 1.0 M sodium hydroxide with a breakaway top section, guard membrane, and cap as shown in Fig. 2.[6]

7.2.2 Heater block assembly, temperature controlled, capable of heating the micro-distillation tubes to 120°C.

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.[7] 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.

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

8.4 *Absorber Solution for MIDI Distillations (0.25 M NaOH)*—Dissolve 10 g NaOH in laboratory water and dilute to 1 L.

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

TABLE 1 Flow Injection Analysis Parameters

FIA Instrument Parameter	Recommended Method Setting
Pump Flow Rates	0.5 to 2 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 versus Ag/AgCl

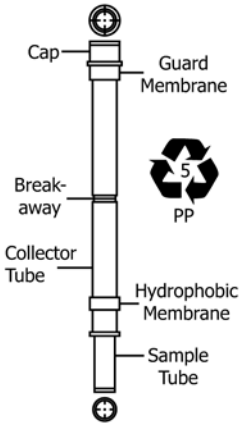

FIG. 2 Micro Distillation Sample Tube

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[4] Both the OI Analytical CN Solution and Lachat Instruments QuikChem Automated Ion Analyzer have been found to be suitable for this analysis.

[5] The sole source of supply of the apparatus known to the committee at this time is PALL Life Sciences Part Number M5PU025, OI Analytical Part Number A0015200, and Lachat Instruments Part Number 50398. 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.

[6] The sole source of supply of the apparatus known to the committee at this time is Lachat Instruments, PN A17001 (subject to US Reg. Patent No. 5,022,967). 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.

[7] *Reagent Chemicals, American Chemical Society Specifications* , 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.

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. (**Warning—**Because KCN is highly toxic, avoid contact or inhalation.)[8]

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 (50, 100, 200, and 500 µg/L CN⁻)*—Pipette 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 1.00 M NaOH (see 8.3). 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 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.9 *Potassium Ferricyanide Stock Solution (1000 µg/mL as CN⁻)*—Weigh 0.2109 g $K_3Fe(CN)_6$ into a 100-mL volumetric flask containing 1 mL 1 M NaOH, then dilute to volume with laboratory water.

8.9.1 *Potassium Ferricyanide Spiking Solution (100 µg/mL CN⁻)*—Pipette 10.0 mL of potassium ferricyanide stock solution into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH, then dilute to volume with laboratory water.

8.10 *Cyanide Electrode Stabilization Solution (Approximately 2 ppm 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.

8.11 *Carrier*—Water as indicated in 8.2.

8.12 *Acidification and Sulfide Abatement Solution*—Weigh 1.00 g bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$, into a 1 L volumetric flask. Add 55 mL of water then carefully add 55 mL of concentrated sulfuric acid to the flask. Gently swirl the flask until the bismuth nitrate pentahydrate has dissolved in the acid solution. Carefully add water to the volumetric flask and fill to volume.

8.13 *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.

8.14 *Lead Acetate Test Strips*—Moisten lead acetate test strips with acetate buffer prior to use.

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

8.16 *Distillation Reagents:*

8.16.1 *Sulfamic Acid*—Dissolve 9.6 g sulfamic acid into a 100-mL volumetric flask partially filled with water. Dilute to volume with water.

8.16.2 *Cyanide Releasing Agent*—Dissolve 16.1 g magnesium chloride hexahydrate, $MgCl_2$-$6H_2O$, into 55.5-mL water. Carefully add 38-mL concentrated sulfuric acid, H_2SO_4, into the solution. The solution will become very hot. Allow the solution to cool prior to use. (**Warning—**Prepare in a fume hood since HCl fumes will be liberated.)

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 Collection and Preservation

10.1 All samples must be collected, preserved, and mitigated for interferences in accordance with Practice D7365.

10.2 For further information on collecting samples refer to Guide D3856.

10.3 The sample must be stabilized at time of collection with the addition of sodium hydroxide (1 M is suitable for pH adjustment) until a pH of 12 to 13 is reached.

10.4 Samples should be stored at 4°C. Samples should be analyzed within 14 days, preferably analyzed as soon as possible to avoid cyanide degradation.

11. Elimination of Interferences

11.1 Cyanide analysis is subject to several potential interferences. Refer to Practice D7365 for the elimination of any known or suspected interferences that may be present in the samples.

11.2 *Sulfide*—The acidification and sulfide abatement solution (8.12) will effectively remove up to 50 mg/L S^{2-} from the distillate. The presence of sulfide above this level can be confirmed with lead acetate test strips previously moistened with acetate buffer (8.13 and 8.14). If the paper turns black,

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[8] Commercially prepared solutions of stock cyanide may be used.

TABLE 2 Precision and Bias in Laboratory Water and Synthetic Wastewater, SM-990-011

NOTE 1—Samples fortified with $K_3Fe(CN)_6$ as CN^-, and results are reported as µg/L (ppb).

Replicate	Water			SM-990-011[A]		
	20 ppb	100 ppb	300 ppb	20 ppb	100 ppb	300 ppb
1	21.5	105	301	23.2	107	284
2	22.0	108	298	22.5	105	300
3	21.7	107	305	23.0	106	306
4	21.7	104	311	22.6	108	305
5	22.1	106	305	22.7	109	306
6	19.4	106	304	22.2	106	320
7	21.8	105	299	22.3	109	305
Std Deviation	0.929	1.35	4.42	0.360	1.57	10.7
Mean	21.5	106	303	22.6	107	304
RSD %	4.33	1.27	1.46	1.59	1.47	3.51
Recovery %	107	106	101	113	107	101

[A] 2 % (volume/volume) synthetic precious metals mining wastewater prepared from SM-990-011, High Purity Standards, Charleston, SC. Prepared sample contains 0.3 mg/L SCN^-, 0.5 mg/L OCN^-, 0.5 mg/L NH_3 as N, and 0.5 ppm NO_3 as N.

TABLE 3 Precision and Bias in Selected Matrices

NOTE 1—Samples fortified with 100 µg/L $K_3Fe(CN)_6$ as CN^-. Results reported in µg/L (ppb).

Sample/Replicate	POTW Effluent[A]	Creek Water	Metals Finishing Wastewater
Background	ND	9.65	8.89
Background	ND	9.79	9.11
Mean Background	0	9.72	9.00
Spike 1	81.2	105	102
Spike 2	89.1	108	103
Spike 3	85.0	108	103
Spike 4	88.6	111	105
Spike 5	87.6	110	106
Spike 6	89.6	108	102
Spike 7	88.6	107	106
Std Deviation	3.01	1.95	1.77
Mean	87.1	108	104
RSD %	3.45	1.80	1.71
Recovery %	87.1	97.3	94.9

[A] POTW = Publicly owned treatment works.
Ascorbic acid added to POTW effluent during sample collection.
ND = not detected.

then sulfide is present and can cause a positive bias. If necessary, dilute the sample prior to the distillation step to avoid interference.

12. Procedure

12.1 Set the controller to 120°C and allow the heater block to warm up to temperature.

12.2 Fill the collector tube of the micro-distillation apparatus (7.2.1) with 1.5 mL of 1.0 M NaOH, and then carefully, place the guard membrane and cap on the top of the tube. When testing multiple samples, fill all of the collector tubes prior to continuing to the next step.

12.3 Place 6.0 mL of sample into the sample tube.

12.4 Pipette 0.25 mL sulfamic acid solution (8.16.1) into the sample tube, then immediately add 0.75 mL cyanide releasing agent (8.16.2) into the sample tube. Immediately after adding the reagents, push the collector tube over the open end of the sample and ensure that the unit is sealed.

12.5 Place the prepared sample tube into the heater block for 30 min.

12.6 After 30 min, remove apparatus from the heater block, and immediately pull off its sample tube with a downward twisting motion. The sample tube should be removed within 4 s or suck back of the sample will occur. (**Warning—**When removing the sample tube from the heater block, wear heat and chemical resistant gloves to prevent thermal and chemical burns.)

12.7 Allow the tubes to cool for at least 10 min, and then tap the collector tubes so that all of the drops of the absorber solution are into the side with the cap. Break away the other side of the collection tube and dilute the distillate to 6 mL with water. The distillate is now ready for analysis.

12.8 Alternatively, if MIDI distillation is utilized, use 50 mL of sample and 50 mL of 0.25 M NaOH as the absorbing solution. Refer to Test Methods D2036.

12.9 Inject each sample distillate into the flow injection apparatus, and inspect for irregular peak shapes, disturbances, or detector overloads. Dilute and re-run samples if necessary.

13. Calibration and Standardization

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

13.2 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 overtighten the pump tubes platens as this will greatly reduce the lifetime of the tubing.

13.3 Aspirate the Cyanide Electrode Stabilization Solution (2 ppm CN^-) from 8.10 into the FIA instrument. 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.

13.4 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.

13.5 Inject each calibration standard (8.8) 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. A second order polynomial is recommended.

13.6 Prepare a new calibration curve at least once daily.

14. Data Analysis and Calculations

14.1 Report the cyanide as parts per billion (µg/L) total cyanide as CN^- using the data acquisition software.

14.2 Multiply the result by any dilution factor and round the test result to three significant figures.

15. Precision and Bias

15.1 The instrumental portion of 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, as described in Practice D2777 – 06. The precision and bias data are shown in Tables 2 and 3.

15.3 An interlaboratory study was conducted in accordance with Practice D2777 – 12 with ten operators in eight laboratories using synthetic effluent and publicly owned treatment works (POTW) effluent samples. The statistical summaries are shown in Tables 4 and 5. The statistical summary for the quality control sample is shown in Table 6.[9]

16. Quality Assurance and Quality Control

16.1 In order to be certain that analytical values obtained using this test method are valid and accurate within the confidence limits of the test, the following QC procedures must be followed when running the test. For a general discussion of quality control and good laboratory practices, see Practice D5847 and Guide D3856.

16.2 *Calibration and Calibration Verification:*

16.2.1 Analyze the calibration standards daily prior to analysis to calibrate the instrument as described in Section 12.

16.2.2 Verify instrument calibration for each analytical batch of 10 samples by analyzing a mid-point standard. The recovery should be 85 to 115 % or else corrective actions should be taken.

16.3 *Initial Demonstration of Laboratory Capability:*

16.3.1 If a laboratory has not performed the test before or if there has been a major change in the measurement system, for example, new analyst, new instrument, etc., a precision and bias study must be performed to demonstrate laboratory capability.

16.3.2 Analyze seven replicates of a standard solution prepared from an independent reference material (IRM) containing 100 µg/L total cyanide prepared from $K_3Fe(CN)_6$. The matrix of the solution should be equivalent to a solution used in the validation study. Each replicate must be taken through the complete analytical procedure. The replicates may be interspersed with samples.

16.3.3 Calculate the mean and standard deviation of the seven values. Refer to Test Method D5847 for information on applying the F test in evaluating the acceptability of the standard deviation.

16.4 *Laboratory Control Sample (LCS):*

16.4.1 To ensure that the test method is in control, analyze a cyanide recovery solution prepared from potassium ferricyanide spiking solution (8.9). The recoveries should be 85 to 115 % or else corrective actions should be taken.

16.5 *Method Blank:*

16.5.1 Analyze a method blank with each batch of samples.

16.5.2 The measured concentration of total cyanide must be less than 2 µg/L. If the concentration is found above this level, analysis of samples is halted until the contamination is eliminated and a blank shows no contamination at or above this level, or the results should be qualified with an indication that they do not fall within the performance of the test method.

16.6 *Matrix Spike (MS):*

16.6.1 To check for interferences in the specific matrix being tested, perform an MS on at least one sample from each batch by spiking an aliquot of the sample with a known concentration of cyanide from $K_3Fe(CN)_6$ and taking it through the analytical method. The spike must produce a concentration in the spiked sample 2 to 5 times the background concentration or 100 µg/L cyanide, whichever is greater. For example, to prepare a 100 µg/L CN^- spike, add 100 µL of potassium ferricyanide spiking solution (8.9.1) to 100 mL sample.

16.6.2 If the recovery is not within 80–120 % or within the limits described in Practice D5847, a matrix interference may be present in the sample selected for spiking. Under these circumstances, one of the following remedies must be employed: the matrix interference must be removed, all samples in the batch must be analyzed by a test method not affected by the matrix interference, or the results should be qualified with an indication that they do not fall within the performance criteria of the test method.

16.7 *Duplicate:*

16.7.1 To check the precision of sample analyses, analyze a sample in duplicate with each batch. If the concentration is less than five times the detection limit, an MS duplicate (MSD) should be used.

16.7.2 Calculate the standard deviation of the duplicate values and compare to the single operator precision from the

TABLE 4 Final Statistical Summary for POTW Effluent

Sample	2	5	6	11	3	9
Number of Usable Values	10	9	10	10	10	10
True Correction, C, µg/L	8.26	10.3	112	120	371	450
Mean Recovery, XBAR	8.57	11.0	106	114	345	409
Percent Recovery	104	106	94.9	94.7	93.0	90.8
Overall Standard Deviation, S_t	1.29	1.70	7.43	9.64	17.7	32.4
Overall Relative Standard Deviation, %	15.1	15.1	7.01	8.46	5.13	7.92
Number of Usable Pairs	9	. . .	10	. . .	10	. . .
Single Operator Standard Deviation, S_o	0.816	. . .	3.40	. . .	19.9	. . .
Single Operator Relative Standard Deviation, %	8.35	. . .	3.08	. . .	5.26	. . .

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[9] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1191. Contact ASTM Customer Service at service@astm.org.

TABLE 5 Final Statistical Summary for Synthetic Effluent

Sample	8	12	1	10	4	7
Number of Usable Values	10	10	10	10	8	10
True Correction, C, µg/L	12.5	15.2	59.4	69.3	370	380
Mean Recovery, XBAR	13.1	14.9	58.0	66.2	342	349
Percent Recovery	105	97.7	97.6	95.6	92.4	91.9
Overall Standard Deviation, S_t	1.74	2.94	4.45	6.57	16.3	14.9
Overall Relative Standard Deviation, %	13.3	19.7	7.67	9.92	4.77	4.27
Number of Usable Pairs	10	. . .	10	. . .	8	. . .
Single Operator Standard Deviation, S_o	1.80	. . .	2.96	. . .	9.32	. . .
Single Operator Relative Standard Deviation, %	12.87	. . .	4.77	. . .	2.70	. . .

TABLE 6 Final Statistical Summary for Quality Control Sample

Number of Usable Values (4 Reps per Operator)	40[A]
True Correction, C, µg/L	165
Mean Recovery	157
Overall Standard Deviation, S_t	9.88
Overall Relative Standard Deviation, %	6.29
Single Operator Standard Deviation, S_o[A]	7.90
Single Operator Relative Standard Deviation, %	5.03

[A] Overall standard deviation equivalent to a single analysis per lab was calculated in accordance with Practice E691, based on the root of the sum of reproducibility and repeatability variances.

collaborative study using an F test. Refer to 6.5.5 of Practice D5847 for information on applying the F test.

16.7.3 If the result exceeds the precision limit, the batch must be reanalyzed or the results must be qualified with an indication that they do not fall within the performance criteria of the test method.

16.8 *Independent Reference Material:*

16.8.1 In order to verify the quantitative value produced by the test method, analyze an IRM submitted as a regular sample (if practical) to the laboratory at least once per quarter. The concentration of the reference material should be in the range of this test method. The value obtained must fall within the control limits specified by the outside source.

16.9 The analyst is permitted certain options to improve the performance of this test method, provided that all performance specifications are met. Any time such modifications are made, the initial demonstration of proficiency must be successfully repeated.

17. Keywords

17.1 amperometry; cyanide; distillation; flow injection analysis; gas diffusion membrane; total cyanide