



Designation: D7284 – 20

Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection¹

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 $\mu\text{g/L}$ (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, health, and environmental 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.*

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. 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,

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 flow-cell 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 $\mu\text{g/L } CN^-$.

7. Apparatus and Instrumentation

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

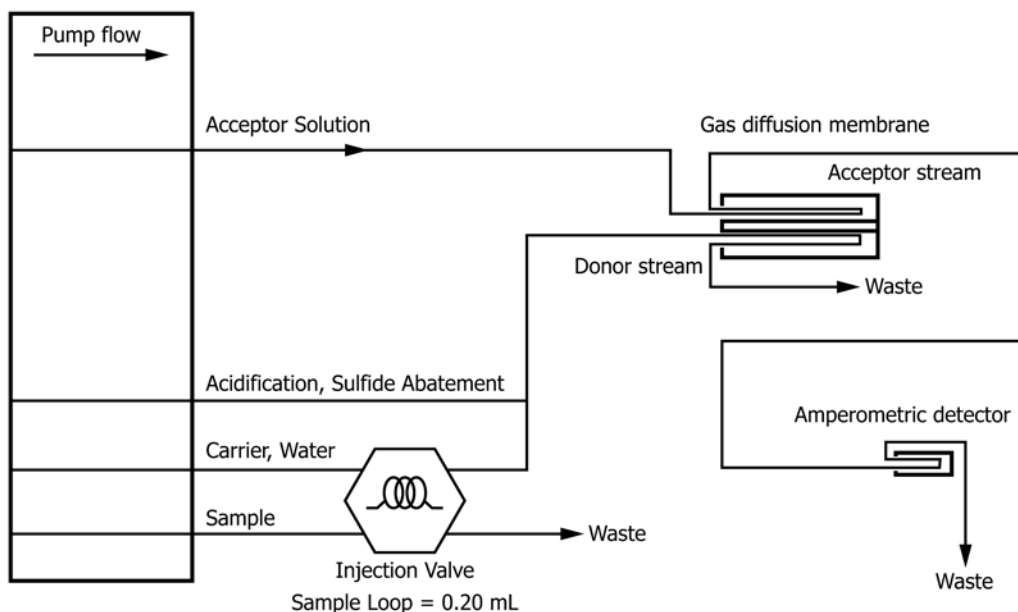


FIG. 1 Flow Injection Analysis Apparatus

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 break-away 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.

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 ACS Reagent Chemicals, *Specifications and Procedures for Reagents and Standard-Grade Reference Materials*, 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.

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.

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

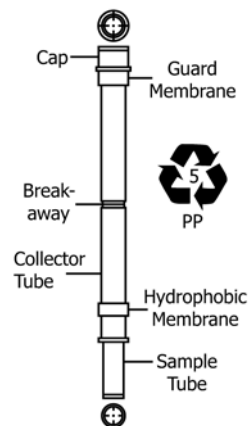


FIG. 2 Micro Distillation Sample Tube

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 K₃Fe(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(NO₃)₃ · 5H₂O, 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 (NaC₂H₃O₂ · 3H₂O) 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, MgCl₂·6H₂O, into 55.5-mL water. Carefully add 38-mL concentrated sulfuric acid, H₂SO₄, 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.)

8.17 *pH Indicator Test Strips*—pH indicator test strips capable of changing color at 0.5 pH units in the range of pH 2 to 12. More than one test strip may be necessary to cover this range.

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 Treat the sample immediately upon sample collection using any of the techniques described in Practice [D7365](#) to mitigate interference, followed by adjustment of the sample to pH > 10 and refrigeration between its freezing point and 6°C. Preserve the sample immediately (within 15 minutes of collection or treatment) by adding 1 mL of 1 M NaOH ([8.3](#)) per litre of sample, and then verify that the pH is greater than pH 10 with indicator test strips ([8.17](#)). If necessary, continue to add sodium hydroxide solution drop wise until the pH is greater than pH 10 being careful not to add excess. See Practice [D7365](#) if the cyanide concentration would change as a result of the addition of NaOH.

⁸ Commercially prepared solutions of stock cyanide may be used.