



Designation: D7511 – 09^{ε2}

Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection¹

This standard is issued under the fixed designation D7511; 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.

^{ε1} NOTE—A typographical error was editorially corrected in Section 8.13 in March 2010.

^{ε2} NOTE—Research report information was editorially added in March 2010.

1. Scope

1.1 This method is used for determining total cyanide in drinking and surface waters, as well as domestic and industrial wastes. Cyanide ion (CN⁻), hydrogen cyanide in water (HCN(aq)), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, silver, and iron may be determined by this method. Cyanide ions from Au(I), Co(III), Pd(II), and Ru(II) complexes are only partially determined.

1.2 The method detection limit (MDL) is 1.0 µg/L cyanide and the minimum level (ML) is 3 µg/L. The applicable range of the method is 3 to 500 µg/L cyanide using a 200-µL sample loop. Extend the range to analyze higher concentrations by sample dilution or changing the sample loop volume.

1.3 This method can be used by analysts experienced with equipment using segmented flow analysis (SFA) and flow injection analysis (FIA) or working under the close supervision of such qualified persons.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Note 2 and Section 9.

2. Referenced Documents

2.1 ASTM Standards:²

D1129 Terminology Relating to Water

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.

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

D3370 Practices for Sampling Water from Closed Conduits

D3856 Guide for Good Laboratory Practices in Laboratories Engaged in Sampling and Analysis of Water

D4210 Practice for Intralaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data³

D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis

D6696 Guide for Understanding Cyanide Species

D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide

3. Terminology

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

3.1.1 *total cyanide*—refers to all cyanide-containing compounds in a sample, including free cyanide, WAD cyanide compounds, and strong metal cyanide complexes.

4. Summary of Test Method

4.1 Prior to analysis, treat the sample to remove potential interferences (Sections 4 and 8). Ultraviolet (UV) digestion releases cyanide from cyanide complexes. Acid addition converts cyanide ion to hydrogen cyanide gas (HCN), which passes under a gas diffusion membrane. The hydrogen cyanide gas diffuses through the membrane into an alkaline receiving solution, where it converts back to cyanide ion. A silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode at an applied potential of zero volt amperometrically monitor the cyanide ion. The current generated is proportional to the cyanide concentration present in the original sample.

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

4.2 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 wastewaters and surface waters.⁴

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

5.3 The method may be used for process control in wastewater treatment facilities.

5.4 The spot test outlined in Test Methods **D2036**, Annex A1 can be used to detect cyanide and thiocyanate in water or wastewater, and to approximate its concentration.

6. Interferences

6.1 Method interferences can be caused by contaminants in the reagents, reagent water, glassware, etc., which may bias the results. Take care to keep all such items free of contaminants.

6.2 Sulfide and sulfide-containing compounds are positive interferents in this method. When acidified, sulfide forms hydrogen sulfide, which passes through the gas diffusion membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time. Treat samples containing sulfide according to Section 11.4. During UV digestion, some sulfur compounds may produce sulfide. TA2 reagent contains a sulfide scrubber that can remove up to 50 mg/L S^{2-} from the system prior to amperometric detection.

6.3 Treat sample containing water-soluble aldehydes, such as formaldehyde or acetaldehyde, by adding ethylenediamine solution.

6.4 Remove oxidizing agents that decompose cyanides by adding ascorbic acid, or sodium arsenite.

6.5 Thiocyanate can produce positive interference when they decompose to cyanide by UV irradiation or oxidation. This method uses 312 nm as the irradiation wavelength, which keeps thiocyanate interference from UV irradiation minimal. Use of Total Acid Reagent–Modified, TA1M (see 8.21) minimizes interference from thiocyanate.

6.6 High concentrations of carbonate can result in a negative response in the amperometric detector when carbon dioxide diffuses across the gas diffusion membrane into the

alkaline receiving solution, reducing its pH. Treat effluents from high carbonate containing wastes, such as coal gasification waste and atmospheric emission scrub water, with hydrated lime to stabilize the sample.

6.7 High concentrations of surfactants interfere by changing the characteristics of the gas diffusion membrane, allowing acid solution to pass through the membrane and enter the detector.

6.8 Nitrate and nitrite if treated with sulfamic acid do not interfere in this method.

6.9 Sodium sulfite, sulfur dioxide, or sodium bisulfite do not interfere at up to 2000 ppm SO_3^- .

6.10 Sodium Thiosulfate exhibits a slight positive bias at concentrations above 200 ppm. This positive bias may be removed by increasing the amount of Bismuth Nitrate in the TA2 reagent.

6.11 Samples containing particulates should be filtered prior to analysis. Extract and combine filtered extract with original sample prior to analysis, or measure the filtered extract and the aqueous sample separately and combine results mathematically.

7. Apparatus

7.1 The instrument should be equipped with a precise sample introduction system, a UV digester with a 312-nm lamp and TFE-effluorocarbon digestion coil, a gas diffusion manifold with hydrophobic membrane, and an amperometric detection system to include a silver working electrode, an Ag/AgCl reference electrode, and a Pt or stainless steel counter electrode. Examples of the apparatus schematics are shown in Fig. 1. Example instrument settings are shown in Table 1.⁵

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.

⁴ 40 CFR Part 136.

⁵ The sole source of supply of the apparatus known to the committee at this time is the trademarked CNSolution equipped with an amperometric flow cell, gas diffusion, and UV digestion module, available from OI Analytical. 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.

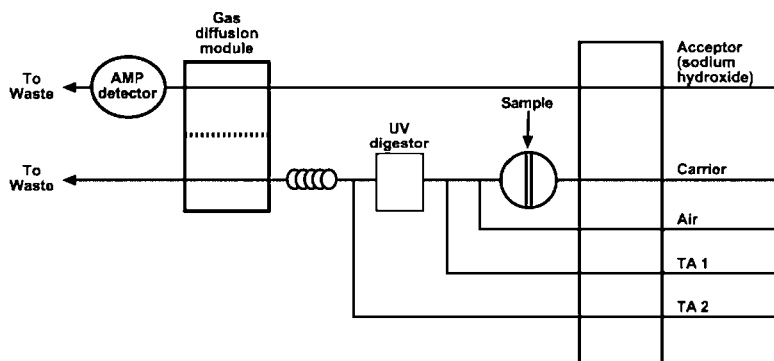


FIG. 1 Flow Injection Analysis Apparatus 1



TABLE 1 Flow Injection Analysis Parameters

FIA Instrument Parameter	Recommended Method Setting
Pump Flow Rates	0.5 to 2 mL/min
Cycle period (total)	90 to 250 s/sample
Sample load period	At least enough time to completely fill the sample loop
Reagent water rinse time between samples	At least 15 seconds
Peak Evaluation	Peak height or area
Working Potential	0.0 V vs Ag/AgCl

7.2 An autosampler is recommended but not required to automate sample injections and increase throughput. Auto samplers are usually available as an option from the instrument's manufacturer.

7.3 *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.

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

7.5 *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.⁶

7.6 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.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 interference free reagent water conforming to Type I or Type II grade of Specification D1193.

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

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

8.5 *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 8.5.1–8.5.4. Store the

solution under refrigeration and check concentration approximately every 6 months and correct if necessary.⁸

NOTE 2—**Warning:** Because KCN is highly toxic, avoid contact or inhalation.

8.5.1 Pipet 100 mL of Stock Cyanide Solution (see 8.5) into a 250 mL flask or beaker.

8.5.2 Add 0.5 mL of rhodanine indicator solution (see 8.17).

8.5.3 Titrate with standardized silver nitrate solution (see 8.18 and 8.18.2) to the first color change from yellow to salmon pink.

8.5.4 Record the results of the titration and calculate the cyanide concentration of the Stock Cyanide Solution according to the equation in 8.18.2.

8.5.5 Use the actual calculated cyanide concentration in all subsequent calculations of working standard concentrations.

8.6 *Intermediate Cyanide Standards:*

8.6.1 *Intermediate Standard 1 (100 µg/mL CN⁻)*—Pipette 10.0 mL of stock cyanide solution (see 8.5) 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.

8.6.2 *Intermediate Cyanide Solution 2 (10 µg/mL CN⁻)*—Pipette 10.0 mL of Intermediate Cyanide Solution 1 (see 8.6.1) 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.

8.7 *Working Cyanide Calibration Standards*—Prepare fresh daily as described in 8.7.1 and 8.7.2 ranging in concentration from 3 to 500 µg/L CN⁻.

8.7.1 *Calibration Standards (20, 50, 100, 200, and 500 µg/L CN⁻)*—Pipette 20, 50, 100, 200, and 500 µL of Intermediate Standard 1 (see 8.6.1) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.7.2 *Calibration Standards (3 and 10 µg/L CN⁻)*—Pipette 30 and 100 µL of Intermediate Cyanide Solution 2 (see 8.6.2) into separate 100 mL volumetric flasks containing 1.0 mL of 1.00 M NaOH (see 8.3). Dilute to volume with laboratory water.

8.8 *Cyanide Electrode Stabilization Solution (Approximately 5 ppm as CN⁻)*—Pipette 500 µL of Stock Cyanide (see 8.5) 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.

8.9 *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.

8.10 *Iron (II) Cyanide Stock Solution*—Weigh 0.2706 g K₄[Fe(CN)₆]·3H₂O into a 100 mL volumetric flask. Place 1.0 mL of 1.00 M NaOH (see 8.3) in the flask and dilute to volume with laboratory water. The solution must be stored in an amber glass bottle under refrigeration at 4°C.

8.11 *Iron (II) Cyanide Intermediate Solution*—Pipet 10.0 mL of the iron (II) cyanide stock solution (see 8.10) into a 100 mL volumetric flask containing 1.0 mL of 1.00 M NaOH (see

⁶ The sole source of supply of the apparatus known to the committee at this time is OI Analytical Part Number A001520 and Pall Corporation Part Number M5PU025. 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 *Annual 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 Commercially available stock cyanide solutions may be substituted.