



Designation: D6888 – 16 (Reapproved 2023)

Standard Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection¹

This standard is issued under the fixed designation D6888; 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 available inorganic cyanide in an aqueous wastewater or effluent. The method detects the cyanides that are free (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions. The method does not detect the less toxic strong metal-cyanide complexes, cyanides that are not “amenable to chlorination.”

1.2 Total cyanide can be determined for samples that have been distilled as described in Test Methods [D2036](#), Test Method A, Total Cyanides after Distillation. The cyanide complexes are dissociated and absorbed into the sodium hydroxide capture solution, which can be analyzed with this test method; therefore, ligand exchange reagents from [8.12](#) and [8.13](#) would not be required when determining total cyanide after distillation.

1.3 This procedure is applicable over a range of approximately $2\text{ }\mu\text{g/L}$ to $400\text{ }\mu\text{g/L}$ (parts per billion) available cyanides. Higher concentrations can be analyzed by dilution or lower injection volume.

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, 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.

1.6 *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 Recom-*

mendations 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](#)
- [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](#)
- [D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide](#)

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 *available cyanides, n*—Inorganic cyanides that are free (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions.

3.2.1.1 *Discussion*—Available cyanide does not include the less toxic strong metal-cyanide complexes, cyanides that are not “amenable to chlorination” and includes weak acid dissociable or weak and dissociable (WAD) cyanides for use in the implementation of International Cyanide Management Code.

4. Summary of Test Method

4.1 Complex cyanides bound with nickel or mercury are released by ligand displacement by the addition of a ligand displacement agent, when necessary.

4.2 Other weak and dissociable cyanide species do not require ligand displacement.

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.

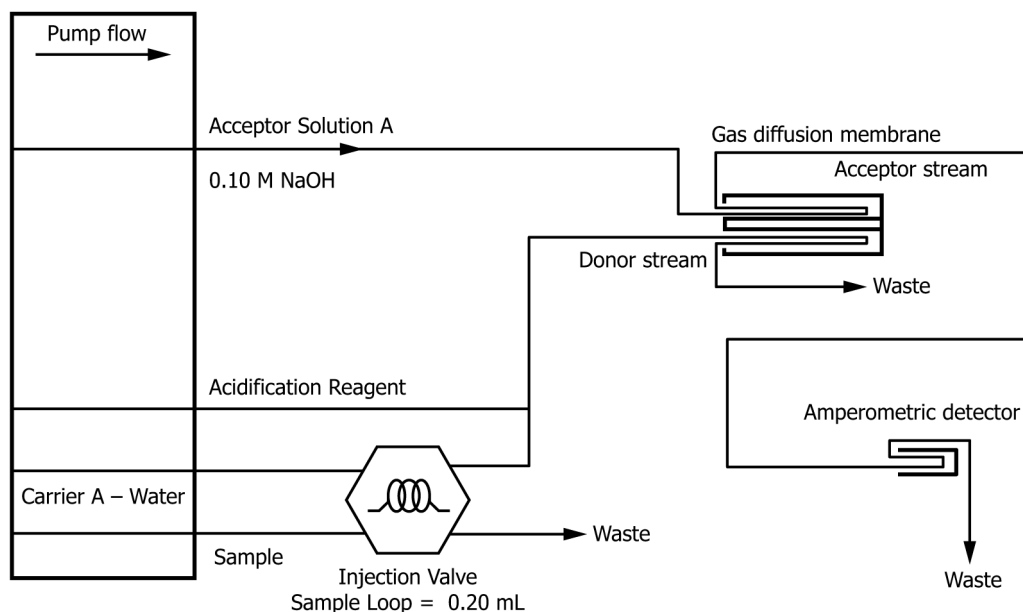


FIG. 1 Flow Injection Analysis Apparatus 1

4.3 The sample 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.

4.4 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 in the standard or sample injected.

4.5 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 water, saline waters, metallurgical process solutions, and wastewater effluent.

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

6. Interferences

6.1 High levels of carbonate can release CO₂ into the acceptor stream and cause an interference with the amperometric detector that result in a slight masking effect (15 % negative bias with 20 ppb cyanide in 1500 ppm carbonate). Refer to 11.2 for sample pretreatment.

6.2 Sulfide above 50 mg/L 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 Practice D7365 for sulfide removal procedures.

6.3 Refer to Practice D7365 for further information on mitigating interferences in water samples for the analysis of cyanide.

7. Apparatus

7.1 The instrument should 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. Examples of the apparatus schematics are shown in Figs. 1-3. 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.

7.2 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.

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.

³ 40 CFR Part 136.

⁴ OI Analytical CNSolution 3100, FS3100, or Flow Solution IV and Lachat Instruments QuikChem Automated Ion Analyzer using Method 10-204-00-5-A have been found to be suitable for this analysis. 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.