Designation: ~~D7728 – 11~~ D7728 – 18

Standard Guide for
Selection of ASTM Analytical Methods for Implementation of International Cyanide Management Code Guidance[1]

This standard is issued under the fixed designation D7728; 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 guide is applicable for the selection of appropriate ASTM standard analytical methods for metallurgical processing sites to conform to International Cyanide Management Code guidance for the analysis of cyanide bearing solutions.

1.2 The analytical methods in this ~~practice~~guide are recommended for the sampling preservation and analysis of total cyanide, available cyanide, weak acid dissociable cyanide, and free cyanide by Test Methods D2036, D4282, D4374, D6888, D6994, D7237, D7284, and D7511. ~~The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.~~

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

1.4 *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.*

1.5 *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
~~D1293 Test Methods for pH of Water~~
D1976 Test Method for Elements in Water by Inductively-Coupled Plasma Atomic Emission Spectroscopy
D2036 Test Methods for Cyanides in Water
D3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
D4282 Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion
D4374 Test Methods for Cyanides in Water—Automated Methods for Total Cyanide, Weak Acid Dissociable Cyanide, and Thiocyanate (Withdrawn 2012)[3]
D4840 Guide for Sample Chain-of-Custody Procedures
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~~
D6888 Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D6994 Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection
D6696 Guide for Understanding Cyanide Species

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[1] This ~~practice~~guide 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.

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

D7237 Test Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D7284 Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection
D7365 Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide
D7511 Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection
D7572 Guide for Recovery of Aqueous Cyanides by Extraction from Mine Rock and Soil

2.2 *ISO Standard:*[4]

ISO 17690:2015 Water Quality—Determination of Available Free Cyanide (pH 6) Using Flow Injection Analysis (FIA), Gas Diffusion, and Amperometric Detection

2.3 *Other References:*

International Cyanide Management Code[5]
National Water Quality Criteria for Cyanide[6]

3. Terminology

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

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 *refrigeration, n*—storing the sample between its freezing point and 6°C.

3.2.2 *titratable cyanide, n*—cyanide measured by titration with silver nitrate to a rhodanine or silver electrode end point.

3.2.3 *weak and dissociable (WAD) cyanide, n*—available cyanide and weak acid dissociable cyanides, excluding determination of iron-, gold-, and cobalt-cyanide complexes.

~~3.2.3 *titratable cyanide, n*—cyanide measured by titration with silver nitrate to a rhodanine or silver electrode end point.~~

4. Summary of Guide

4.1 Guidance is provided for selection of the appropriate analytical methods to determine cyanide for to apply to the International Cyanide Management Code guidance for analysis of cyanide in solution.

5. Significance and Use

5.1 This guide is intended as a means for selecting the proper methods for measuring cyanide to conform to the International Cyanide Management Code guidance related to the analysis of cyanide bearing solutions. Cyanide is analyzed in process solutions and in discharges in order to apply code guidance; however, improper sample collection and preservation can result in significant positive or negative bias, potentially resulting in over reporting or under reporting cyanide releases into the environment.

5.2 This guide contains comparative test methods that are intended for use in routine monitoring of cyanide. It is assumed that all who use methods listed in this guide will be trained analysts capable of performing them skillfully and safely. It is expected that work will be performed in a properly equipped laboratory applying appropriate quality control practices such as those described in Guide D3856.

6. Interferences

6.1 Multiple interferences could affect the cyanide analytical results using methods enumerated in this guide. Refer to Practice D7365 for proper handling of the solutions during sampling, mitigation of interferences and preservation prior to cyanide analysis.

6.2 Unless otherwise specified, samples must be analyzed within 14 days; however, it is recommended to estimate the actual holding time for each new sample matrix as described in Practice D4841. Certain sample matrices may require immediate analysis to avoid cyanide degradation due to interferences. A holding time study is required if there is evidence that cyanide degradation occurs from interferences which would cause the holding time to be less than specified in this ~~practice~~guide or Practice D7365. Potential interferences for cyanide analytical methods are shown in Table 1.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this guide. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where

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[4] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

[5] Available from International Cyanide Management Institute, 1400 I Street, NW, Suite 550, Washington, DC 20005, https://www.cyanidecode.org.

[6] Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

TABLE 1 Summary of CN Method Interferences~~ - adapted from ASTM D7365-09~~

NOTE 1—Adapted from Practice D7365 – 09.

~~ANALYSIS STEP~~ Analysis Step	~~COMPOUND~~Compound	~~PROCESS/~~ Process/ Measurement ~~MEASUREMENT TECHNIQUE~~Technique	~~DESCRIPTION OF~~Description of ~~INTERFERENCE~~Interference
~~Sampling, Preservation, and Storage~~	~~Residual chlorine, peroxide, or other oxidizers~~	~~N/A~~	~~React with cyanide in solution rapidly decreasing the cyanide concentration. Oxidizers can co-exist with cyanide~~
Sampling, Preservation, and Storage	Residual chlorine, peroxide, or other oxidizers	N/A	React with cyanide in solution rapidly decreasing the cyanide concentration. Oxidizers can co-exist with cyanide.
	Chloramines	N/A	React with sample at pH > 10 increasing or decreasing the cyanide concentration
	Sulfide	N/A	Reacts with cyanide and oxygen to form thiocyanate decreasing the cyanide concentration. Reaction is especially rapid if metal sulfides are present.
	Native sulfur (colloidal sulfur)	N/A	Very rapid reaction to form thiocyanate. Decreases the cyanide concentration.
	~~Sulfite~~	~~N/A~~	~~Reacts with cyanide at pH > 10 decreasing the cyanide concentration. Reaction is almost immediate at pH.12~~
	Sulfite	N/A	Reacts with cyanide at pH > 10 decreasing the cyanide concentration. Reaction is almost immediate at pH 12.
	~~Light (<350nm)~~	~~N/A~~	~~Reacts with metal cyanide complexes releasing HCN~~
	Light (<350 nm)	N/A	Reacts with metal cyanide complexes releasing HCN
	~~Ascorbic acid~~	~~N/A~~	~~Reacts with cyanide decreasing the cyanide concentration. Sample holding time with ascorbic acid < 48 hours. In some samples, ascorbic acid can react with ammonia or other nitrogen sources and increase the cyanide concentration.~~
	Ascorbic acid	N/A	Reacts with cyanide decreasing the cyanide concentration. Sample holding time with ascorbic acid <48 hours. In some samples, ascorbic acid can react with ammonia or other nitrogen sources and increase the cyanide concentration.
	~~Formaldehyde~~	~~N/A~~	~~Reacts with cyanide decreasing the concentration. In some samples, formaldehyde reacts with ammonia or other nitrogen sources and increases the cyanide concentration.~~
	Formaldehyde	N/A	Reacts with cyanide decreasing the concentration. In some samples, formaldehyde reacts with ammonia, or other nitrogen sources and increases the cyanide concentration
	Oxidizers	Distillation	React with cyanide decreasing its concentration
	Sulfide	Distillation	Distills into absorber solution and reacts with cyanide to form thiocyanate
		Gas -diffusion	Passes through the diffusion membrane
	Sulfite (or sulfur dioxide)	Distillation	Reacts with cyanide decreasing its concentration. Distills into absorber solution and reacts with cyanide decreasing its concentration.
	~~Thiosulfate and other oxidized sulfur species (except sulfate)~~	~~Distillation~~	~~Decompose to form native sulfur and sulfur dioxide. Reacts with cyanide decreasing its concentration~~
	Thiosulfate and other oxidized sulfur species (except sulfate)	Distillation	Decompose to form native sulfur and sulfur dioxide. Reacts with cyanide decreasing its concentration.
	Thiocyanate	Cyanide Amenable to Chlorination (CATC)	Reacts with chlorine during alkaline chlorination and generates cyanide. Causes negative CATC results.
		~~Distillation~~	~~Decomposes to sulfur dioxide and reacts with cyanide decreasing its concentration. Sulfur dioxide distills into absorber solution.~~
		Distillation	Decomposes to sulfur dioxide and reacts with cyanide decreasing its concentration. Sulfur dioxide distills into absorber solution
		UV Irradiation	Can react at <280 nm to form CN
	~~Thiocyanate + Nitrate or Nitrite~~	~~Distillation~~	~~Decompose to form cyanide.~~
	Thiocyanate + Nitrate or Nitrite	Distillation	Decompose to form cyanide
	~~Misc. organics + Nitrate or Nitrite~~	~~Distillation~~	~~Decompose to form cyanide.~~
	Misc. organics + Nitrate or Nitrite	Distillation	Decompose to form cyanide
	Carbonate	Distillation	Excessive foaming and possible violent release of carbon dioxide