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 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 *This guide 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 guide to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

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 Argon 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
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 Cyanide 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
D7237 Test Method for 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 After Remediation of Process Releases

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, 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 *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.

---

[1] This practice 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.

Current edition approved Sept. 1, 2011. Published September 2011. DOI: 10.1520/D7728–11

[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.

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 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 such specifications are available. 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.[3]

7.2 *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 D1193. Type III or IV water may be used if they do not cause measurable change in the blank or sample.

7.3 *Sample Bottles*—See section 9.2 for further information about sample bottles.

8. Hazards

8.1 **Warning—**Because of the toxicity of cyanide, great care must be exercised in its handling. Acidification of cyanide solutions produces toxic hydrocyanic acid (HCN). Adequate ventilation is necessary when handling cyanide solutions and a fume hood should be utilized whenever possible.

8.2 **Warning—**Many of the reagents used in this guide are highly toxic. These reagents and their solutions and extracted solids must be disposed of properly.

9. Sampling

9.1 Obtain a representative sample of the solution to be tested by using, where available, ASTM sampling methods developed for the cyanide processing industry (see Practice D7365.

9.2 Sampling methodology for materials of similar physical form shall be used where no specific methods are available.

9.3 Laboratory personnel and field samplers should follow the industry best practice or acceptable metallurgical methods for sampling and sample preparation of process solutions.

9.3.1 Refer to Guide D4840 for chain-of-custody procedures.

9.4 *Sample Containers:*

9.4.1 Sample containers shall be made of materials that will not contaminate the sample and bottles need to be cleaned thoroughly to remove all extraneous surface contamination prior to use, if necessary. Chemically resistant rigid plastic containers, such as those made of high-density polyethylene (HDPE) are suitable as well as amber glass containers. Samples should be collected and stored in opaque containers to minimize exposure to ultraviolet radiation and loss of moisture and hydrogen cyanide.

9.5 New, commercially cleaned, containers certified to be free of contamination are recommended for handling solutions; otherwise, wash containers with soap or biodegradable detergent if required, then dry by draining. For further information on sample containers, see Practices D3694.

10. Procedure Selection

10.1 Principles, Standards of Practice and Guidance

10.1.1 The International Cyanide Management Code is organized into principles and standards of practice for implementation using the guidance. Those principles, standards of practice and guidance related to metallurgical processing which require the use of analytical methods are discussed with identification of specific ASTM analytical methods that are appropriate for implementing the guidance.

10.2 Principle- Operations

10.2.1 Manage cyanide process solutions and waste streams to protect human health and the environment.

[3] 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, (http://uk.vwr.com), and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

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

ANALYSIS STEP	COMPOUND	PROCESS/ MEASUREMENT TECHNIQUE	DESCRIPTION OF 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
	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
	Light (<350nm)	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.
	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
	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.
		UV Irradiation	Can react at <280nm to form CN
	Thiocyanate + 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
Measurement	Sulfide	Titration	Detected as Cyanide
		Ion Selective Electrode	Detected as Cyanide
		Colorimetry	Detected as Cyanide (at > 50 mg S/L)
		GD-Amperometry	Detected as Cyanide (at > 50 mg S/L)
	Thiocyanate	Colorimetry	Detected as Cyanide
	Fatty acids	Titration	Mask endpoint
	Sulfur dioxide	Colorimetry	Increase chloramine T demand resulting in negative bias. The increased demand may not be noticed in automated colorimetric methods
	Carbonates	GD-Amperometry	Negative bias at > 1500 mg CO3/L

10.2.1.1 Standard of Practice – Introduce management and operating systems to minimize cyanide use, thereby limiting concentrations of cyanide in mill tailings.

10.2.1.2 Guidance - While facilities must use the amount of cyanide determined to be metallurgically necessary for efficient precious metal extraction, operations should use bottle roll or other test procedures to determine the optimal amount of cyanide, and should re-evaluate and adjust addition rates as necessary when changes in ore type or processing plant practices occur. A summary of ASTM methods is given in Table 2.

(1) Titratable cyanide – Most metallurgical operations and laboratories rely on the silver nitrate titration to estimate the cyanide available for leaching gold, which is standardized in the D2036 Titration Procedure. Measurement units are typically expressed as sodium cyanide, rather than cyanide, in order to track the usage of the commercially available reagent. The solution pH should be adjusted to about 12 prior to titration to assure that the all of the free cyanide is present as the cyanide ion, rather than hydrogen cyanide.

(2) Other techniques that may be used to directly estimate the cyanide in process and laboratory solutions are ion selective electrode (ISE), the ion chromatography (IC), and the free cyanide method in D7237. Users of these techniques will likely need to dilute process samples into the linear range of the method and need to take into account any shifts in equilibrium of metal cyanide complexes resulting from dilution in interpreting the results. Ion Chromatography and Ion Selective

TABLE 2 Summary of ASTM CN Methods

Analyte	Method	Comments
Titratable CN	D2036 (no distillation)	Applicable to leachate solutions when Cu < 50 mg/L. Measures CN > 1mg/L. Adjust to pH 12
	D6888 (no ligands)	Preferred method for leachate solutions when Cu > 50 mg/L Measures Cu, Ni, and Hg complexes
Free Cyanide	D7237	Preferred method
	D4282	Alternate method, provided equivalent results are demonstrated
WAD Cyanide	D6888	Preferred method, quantitative recovery of Zn, Cd, Cu, Ag, Ni, and Hg complexes
	D2036 amenable	Alternate method, provided equivalent results are demonstrated
	D2036 WAD	Alternate method, provided equivalent results are demonstrated
	D4374 WAD	Alternate method, provided equivalent results are demonstrated
Total Cyanide	D7511	Preferred method
	D2036 (with distillation)	Alternate method, provided equivalent results can be demonstrated
	D4374 (UV >290nm)	Alternate method, provided equivalent results can be demonstrated
	D7284	Alternate method, provided equivalent results can be demonstrated

Electrode ASTM methods have only been interlaboratory validated for use in D2036 distillates. There are no ASTM Ion Chromatography, or Ion Selective Electrode methods that have been interlaboratory validated in complex hydrometallurgical process matrices. The free cyanide method, D7237, has been interlaboratory tested for discharge waters, covering the range of 0.002 to 0.5 mg/L cyanide, with a lower scope limit of 0.009 mg/L free cyanide in a chlorinated gold processing discharge matrix.

(3) Convert results to kg NaCN/tonne of solution by multiplying the cyanide result by 0.0019 and to lbs NaCN/ tonne of solution by multiplying the cyanide result by 0.0038.

(4) WAD cyanide methods – Significant quantities of metal cyanide complexes in process solutions (i.e. Cu>50 mg/L) make it difficult to detect the endpoint for the titratable cyanide method. In these cases, it is recommended to determine the WAD cyanide using D 6888 and measure the metals that form cyanide complexes by method D1976 or method D6994. To determine the cyanide concentrations available for gold leaching, cyanide associated with certain metals (e.g. Cu, Ni, Hg, etc.) should be subtracted from the WAD cyanide values.

10.2.1.3 Standard of Practice – Implement measures to protect birds, other wildlife and livestock from adverse effects of cyanide process solutions.

(1) Guidance - Process solutions impounded in a Tailing Storage Facility (TSF), leaching facilities and solution ponds can attract birds, wildlife and livestock. An aqueus concentration of 50 mg/L WAD cyanide or lower is typically viewed as being protective of most wildlife and livestock mortality other than aquatic organisms.

(2) WAD cyanide methods –Method D6888 is recommended for monitoring process solutions. D2036 test method C, or D4374 WAD may also be used if demonstrated that they produce comparable results.

10.2.1.4 Standard of Practice – Implement measures to protect fish and wildlife from direct and indirect discharges of cyanide process solutions to surface water.

(1) Guidance - Discharges to surface waters should not exceed 0.5 mg/l WAD cyanide nor result in a concentration of free cyanide in excess of 0.022 mg/l within the receiving surface water body, and downstream of any mixing zone approved by the applicable jurisdiction. The 0.022 mg/l guideline is from the United States Environmental Protection Agency's National Water Quality Criteria for Cyanide, and represents a concentration to which a freshwater aquatic community can be briefly exposed without resulting in an unacceptable effect.

(2) WAD cyanide methods –D6888 is recommended for monitoring process solutions discharged to surface water. D2036 test method C, or D4374 WAD may also be used if it can be demonstrated that they produce comparable results.

(3) Free cyanide methods – Use of D7237 is recommended for monitoring free cyanide in discharges after the mixing zone. D4282 may also be used if it can be demonstrated to produce comparable results.

(4) Total Cyanide – If total cyanide is regulated, the use of D7511 is recommended to minimize the potential interference from thiocyanate. Other cyanide methods, such as D2036, D4374, and D7284 may be used provided comparable results can be demonstrated.

10.2.1.5 Standard of Practice - Incorporate into response plans monitoring elements and remediation measures that account for the additional hazards of using cyanide treatment chemicals.

(1) Guidance - The Plan should describe specific remediation measures including procedures for the recovery or treatment of solutions or solids, decontamination of soils or other contaminated media and management and/or disposal of spill clean-up debris.

(2) Guide D7572 should be followed to determine the cyanide concentrations in soil or rock possibly contaminated by cyanide process solutions to determine the effectiveness of remediation measures.

11. Keywords

11.1 free cyanide; International Cyanide Management Code; WAD cyanide