INTERNATIONAL

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Standard Guide for Understanding Cyanide Species[1]

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1. Scope

1.1 This guide defines guidance based on a consensus of viewpoints for interpretation of test results to identify various chemical forms of cyanide. It is intended to provide a general understanding of the chemical nature of distinct cyanide species as related to chemical analysis and environmental fate and transport.

1.2 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 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

D1426 Test Methods for Ammonia Nitrogen In Water

D3590 Test Methods for Total Kjeldahl Nitrogen in Water

D6888 Test Method for Available Cyanides with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

D7237 Test Method for Free Cyanide and Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

3. Terminology

3.1 *Definitions*—For a definition of terms used in this guide, refer to Terminology D1129.

4. Significance and Use

4.1 This guide provides standard terminology for use in identifying and describing the different chemical forms of cyanide. The complex nature of cyanide chemistry, existence of numerous distinct chemical forms as well as the various regulatory distinctions that may be made can lead to confusion in technical discussions on cyanide and in the selection of appropriate methods for its analysis. This guide is intended to provide clarification and a common framework of terms and definitions to facilitate discussions and referencing different cyanide chemical species and groups of cyanide compounds.

4.2 The use of such common terminology is particularly important from an environmental perspective because certain forms of cyanide are considered to be toxic. Therefore, their release into the environment is regulated by federal and state agencies. Thus a general understanding of cyanide chemistry and species definitions is needed for proper wastewater management and testing.

5. Cyanide Species Terms and Definitions

5.1 *Chemistry Related Terms and Definitions:*

5.1.1 *Cyanide Ion*—The term used to describe a negatively charged ion comprised of one carbon atom and one nitrogen atom triply bonded to each other ($C{\equiv}N^-$). The cyanide ion is reactive and readily forms neutral compounds or anionic complexes with most metals.

5.1.2 *Free Cyanide*—The form of cyanide that is bioavailable and known for its toxic effect on organisms (**1**).[3] Free cyanide refers to the sum of molecular hydrogen cyanide (HCN) and cyanide ion (CN^-). Hydrogen cyanide is a colorless, poisonous gas having an odor of bitter almonds (mp = -13.4 °C, bp = 25.6 °C). It is readily soluble in water existing as HCN or CN^-, or both, depending on the pH conditions ($pK_a = 9.36$). At a pH of 7 or less in water, free cyanide is present entirely as HCN; the opposite is true at pH 11 or greater. Because of its toxicity, free cyanide is regulated in environmental wastewater discharges.

5.1.2.1 In Test Method D7237, sum of the free cyanide (HCN and CN^-) and cyanide bound in the metal-cyanide

[1] This 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 boldface numbers in parentheses refer to a list of references at the end of this standard.

complexes that are easily dissociated into free cyanide under the test conditions described in Test Method D7237 at pH 6 and room temperature.

5.1.3 *Aquatic Free Cyanide*—In Test Method D7237, free cyanide measured when the buffer or temperature is adjusted to mimic the receiving water environment.

5.1.4 *Simple Cyanide*—A neutral compound comprised of an alkali metal, alkaline earth metal or ammonium cation bound to cyanide. Simple cyanides are so named because of their structural simplicity and their ability to completely dissolve and dissociate in water to produce free cyanide and a cation according to the following reaction:

$$ACN \rightarrow A^{+} + CN^{-} \quad (1)$$

where:

A = alkali metal, alkaline earth metal or ammonium cation.

Examples of simple cyanides include sodium cyanide (NaCN) and potassium cyanide (KCN).

5.1.5 *Metal Cyanide Complex*—A negatively charged ionic complex consisting of several cyanide ions bound to a single transition metal cation. Also referred to as "metal-complexed cyanides," "metal cyano-complexes" or "transition metal cyanides," these species have the general formula:

$$[M(CN)_b]^{x-} \quad (2)$$

where:

M = transition metal cation,
b = number of cyanide groups, and
x = ionic charge of the transition metal complex.

Metal cyanide complexes are represented by the following equilibrium in aqueous solution:

$$[M(CN)_b]^{x-} \Leftrightarrow M^{n+} + bCN^{-} \quad (3)$$

where:

M = transition metal cation,
n = ionic charge of the transition metal cation,
b = number of cyanide ions, and
x = ionic charge of the transition metal complex.

The degree of dissociation of the metal cyanide complex is dependent of the stability of the complex and the solution pH. On this basis, metal cyanide complexes are divided into two categories: (*1*) "weak acid dissociable metal cyanide complexes" and (*2*) "strong acid dissociable metal cyanide complexes."

5.1.5.1 *Weak and Dissociable Metal Cyanide Compounds and Complexes*—A cyanide compound or complex that either dissociates under conditions of weak acid distillation, pH buffering, or ligand-exchange reagents. Because of their ability to dissociate under slightly acidic or slightly basic to nearly neutral, ambient conditions, or through the use of ligand-exchange reagents, the weak and dissociable metal cyanide compounds and complexes are sometimes regulated along with free cyanide in wastewater discharges. Several weak and dissociable metal cyanide compounds and complexes are presented in Table 1. A weak and dissociable metal cyanide compound or complex is also sometimes referred to as a "weakly complexed cyanide," "dissociable cyanide," "available cyanide," "directly toxic cyanide," etc.

TABLE 1 Selected Weak Acid Dissociable Metal Cyanide Compounds and Complexes (2)

Metal Cyanide Complex	Stability Constant (log K at 25 °C)
$[Hg(CN)_4]^{2-}$ [A]	6.22
$Hg(CN)_2$ [B]	32.8
$[Cd(CN)_4]^{2-}$	17.9
$[Zn(CN)_4]^{2-}$	19.6
$[Ag(CN)_2]^{-}$	20.5
$[Cu(CN)_4]^{3-}$	23.1
$[Ni(CN)_4]^{2-}$	30.2

[A] Refers to the stepwise dissociation: $[Hg(CN)_4]^{2-} \Leftrightarrow Hg(CN)_2 + 2CN^{-}$.
[B] $Hg(CN)_2$ will be recovered by the available cyanide method (5.2.8) provided that ligand-exchange reagents are used.

(1) Weak Acid Dissociable Metal Cyanide Compounds and Complexes—A cyanide compound or complex that dissociates under mildly acidic conditions (pH = 3–6) and in dilute solutions, forming free cyanide. Complex cyanides bound with cadmium, zinc, silver and copper typically dissociate under mildly acidic distillation conditions.

(2) Ligand Exchange Dissociable Metal Cyanide Compounds and Complexes—A cyanide compound or complex that dissociates under the action of ligand-exchange reagents and gas diffusion conditions (see Test Method D6888). Complex cyanides bound with nickel or mercury typically require ligand-exchange reagents for dissociation.

(3) pH Buffering Dissociable Metal Cyanide Compounds and Complexes—A cyanide compound or complex that dissociates under the action of pH buffering, forming free cyanide (see Test Method D7237). Simple cyanides bound with sodium and complex cyanides bound with zinc or cadmium are amenable to dissociation using pH 6–8 buffer.

5.1.5.2 *Strong Metal Cyanide Complex*—A metal cyanide complex that requires strongly acidic conditions (pH <2) in order to dissociate and form free cyanide. Due to their resistance to dissociation and subsequent low toxicity, the strong metal cyanide complexes are distinguished on a regulatory basis from other forms of cyanide. Although some of the strong metal cyanide complexes are also subject to photochemical dissociation when exposed to UV radiation, the rate of dissociation is generally low in naturally turbid, shaded surface waters. In addition, volatilization and biodegradation of any dissociated free cyanide typically prevents their accumulation to toxic levels in the environment thus supporting this regulatory distinction. The term "strongly complexed cyanide" is also sometimes used to describe a strong metal cyanide complex. The most prevalent and well known of such species are the iron cyanide complexes namely, ferrocyanide [IUPAC nomenclature: hexacyanoferrate(II) ion] and ferricyanide [IUPAC nomenclature: hexacyanoferrate(III) ion; IUPAC = International Union of Pure and Applied Chemistry] as well as gold and cobalt cyanide complexes. Examples of strong metal cyanide complexes are presented in Table 2.

5.1.6 *Metal-Metal Cyanide Complex Salts*—Neutral compounds comprised of one or more metal cations and an anionic cyanide complex. The metal cations balance the charge of the anionic complex thus creating a neutral species. These species are divided into two categories: (*1*) "alkali metal-metal cyanide