



Standard Guide for Understanding Cyanide Species¹

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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.

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

D7237 Test Method for 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). 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 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:



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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.

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:



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:



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 Acid Dissociable Metal Cyanide Complex—A cyanide complex that dissociates under mildly acidic conditions (pH = 3-6) and in dilute solutions, forming free cyanide. Because of their ability to dissociate under slightly acidic to nearly neutral, ambient conditions, the weak acid dissociable metal cyanide complexes are sometimes regulated along with free cyanide in wastewater discharges. Several weak acid dissociable metal cyanide complexes are presented in Table 1. A weak acid dissociable metal cyanide 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 Complexes (2)

Metal Cyanide Complex	Stability Constant (log K at 25°C)
$[Hg(CN)_4]^{2-}$ ^A	6.22
$[Cd(CN)_4]^{2-}$	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: $[Hg(CN)_4]^{2-} \rightleftharpoons Hg(CN)_2 + 2CN^-$.

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 complex salts” or “alkaline earth metal-metal cyanide complex salts” and (2) “transition metal-metal cyanide complex salts”.

5.1.6.1 Alkali Metal-Metal Cyanide Complex Salts—Compounds comprised of one or more alkali metal cations and an anionic cyanide complex having the general formula:



where:

A = alkali metal counter cation,

a = number of alkali metal counter cations,

M = transition metal cation,

b = number of cyanide ions, and

y = number of waters of crystallization.

Alkali metal-metal cyanide complex salts readily dissolve in water to form a free alkali metal cation and an anionic metal cyanide complex as follows:

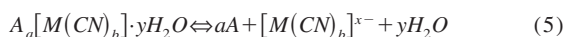
TABLE 2 Selected Strong Metal Cyanide Complexes (2, 3)

Cyanide Complex	Stability Constant (log K at 25°C)
$Hg(CN)_2$ ^{A,B}	32.8
$[Fe(CN)_6]^{4-}$	35.4
$[Au(CN)_2]^-$	37 ^C
$[Fe(CN)_6]^{3-}$	43.6
$[Co(CN)_6]^{3-}$	64 ^C

^A $Hg(CN)_2$ is actually a neutral species and therefore more correctly identified as a metal cyanide compound rather than a metal cyanide complex.

^B $Hg(CN)_2$ will be recovered by the available cyanide method (5.2.8) provided that ligand-exchange reagents are used.

^C This stability constant is considered to be an estimate.



where:

- A = alkali metal counter cation,
- a = number of alkali metal counter cations,
- M = transition metal cation,
- b = number of cyanide ions,
- x = ionic charge of the transition metal complex, and
- y = number of waters of crystallization.

5.1.6.2 Alkaline Earth Metal-Metal Cyanide Complex Salts—Structurally and chemically similar to alkali metal-cyanide complex salts, these compounds contain an alkaline earth metal cation in place of an alkali metal cation (see 5.1.6.1).

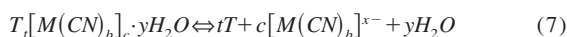
5.1.6.3 Transition Metal-Metal Cyanide Complex Salts—Compounds consisting of one or more transition metal cations and an anionic metal cyanide complex having the general formula:



where:

- T = transition metal counter cation,
- t = number of transition metal counter cations,
- M = transition metal cation,
- b = number of cyanide ions,
- c = number of metal complex anions, and
- y = number of waters of crystallization.

Transition metal-metal cyanide complex salts, also referred to as “double metal cyanide complex salts” when the counter ion and the metal cation bonded to the cyanide ligands are the same, are extremely stable and generally insoluble under acidic and neutral pH conditions (4-6). They are, however, soluble under alkaline conditions. Dissolution into aqueous solution is represented by the following equilibrium:



where:

- T = transition metal counter cation,
- t = number of transition metal counter cations,
- b = number of cyanide ions,
- c = number of metal complex anions,
- x = ionic charge of the transition metal complex, and
- y = number of waters of crystallization.

An example of a transition metal-metal cyanide complex salt is the ferric ferrocyanide species [IUPAC nomenclature: iron(III) hexacyanoferrate(II)] known as prussian blue: $Fe_4[Fe(CN)_6]_3$.

NOTE 1—Metal cyanide complexes that contain other ligands besides cyanide may also exist in aqueous solution. Examples of such complexes include: $Hg(OH)CN$ and $[Fe(CN)_5H_2O]^{3-}$ (7).

5.2 Operationally Defined Definitions:

5.2.1 Inorganic Cyanide—This category includes all inorganic compounds or ionic complexes containing one or more cyanide ligands bonded directly to either a metal or an ammonium ion.

5.2.2 Organic Cyanide—Organic compounds containing a cyanide functional group. Examples of naturally occurring organic cyanides are the cyanogenic glycosides. These species

are comprised of a cyanide group bound to a carbon atom that is in turn bound by a glycosidic linkage to one or more sugars as depicted in Fig. 1. Specific examples of naturally occurring organic cyanides include linamarin, dhurrin, and amygdalin (Fig. 2). Organic cyanides also include nitriles, which are commercially prepared, substituted hydrocarbons such as acetonitrile (CH_3CN) or cyanobenzene (C_6H_5CN). Because the chemical bond to the cyanide functional group in organic cyanides is very stable, free cyanide is generally not released from organic cyanides in aqueous solution under normal ambient conditions.

5.2.3 Total Cyanide—Total cyanide is an analytically defined term that refers to the sum total of all of the inorganic chemical forms of cyanide that dissociate and release free cyanide when refluxed under strongly acidic conditions. Total cyanide is determined analytically through strong acid distillation or UV irradiation followed by analysis of liberated free cyanide (8-10) on aqueous samples preserved with NaOH (pH ~ 12). In water, total cyanide includes the following dissolved species: free cyanide, weak acid dissociable metal cyanide complexes and strong metal cyanide complexes. However, it should be noted that because of the sample preservation, certain suspended or colloidal forms of cyanide will dissolve prior to the distillation step; the recovery of which during the acid distillation step is variable and depends on various solution parameters, such as cyanide concentration in suspended solids, ionic strength of the sample, sample temperature, acid digestion times, and so forth. Also, some of the strong metal cyanide complexes, such as those of gold, cobalt and platinum, might not be fully recovered during the total cyanide analytical procedure. Additionally, total cyanide may also include some organic forms of cyanide such as nitriles that may release free cyanide under the conditions of the analysis.

5.2.4 Cyanides—This term as used by the U.S. Environmental Protection Agency, and appears as a Clean Water Act (CWA) pollutant as Item No. 23 in the list of toxic pollutants pursuant to Section 307(a)(1) of the CWA (11). The operational methods employed by the EPA for this category are listed in 40 CFR Part 136 (12).

5.2.5 Diffusible Cyanide—The form of operationally defined cyanide that diffuses as HCN gas at room temperature and at a pH of 6. Diffusible cyanide is recovered and determined using microdiffusion analysis (10). In water, this form of cyanide generally includes dissolved free cyanide.

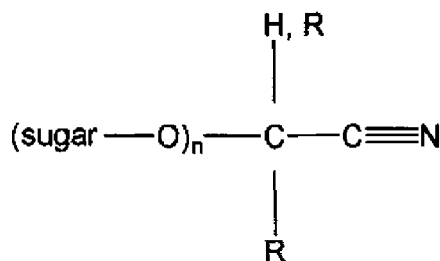


FIG. 1 Cyanogenic Glycoside General Structure

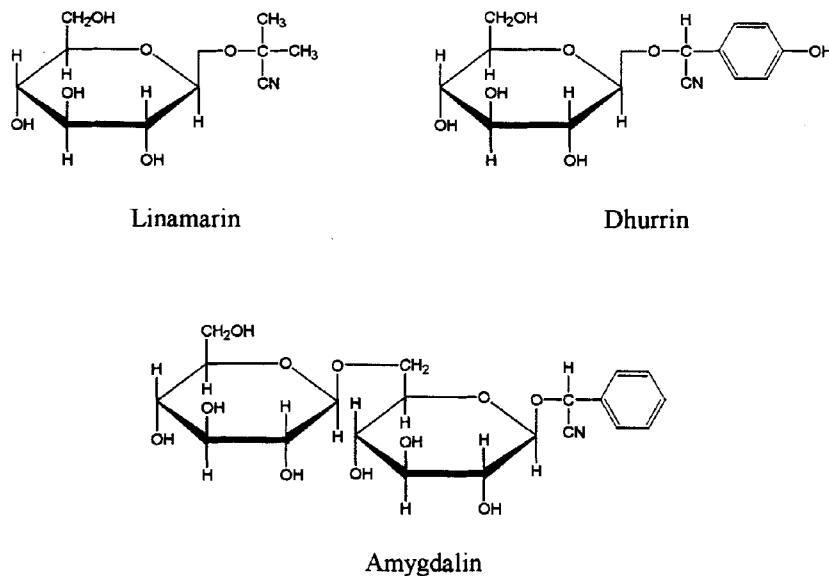


FIG. 2 Examples of Cyanogenic Glycosides

Because of this, diffusible cyanide may provide a relatively accurate estimate of cyanide toxicity.

5.2.6 Cyanides Amenable to Chlorination (CATC)—A class of operationally defined cyanide species that undergo dissociation and oxidation when exposed to chlorine under alkaline conditions. These species are determined analytically by computing the difference in total cyanide of an untreated sample and a sample treated with chlorine at room temperature (8-10). In water, this group of cyanide species generally includes free cyanide and the weak acid dissociable metal cyanide complexes. Cyanides amenable to chlorination provides a conservative estimate of toxicity because, in addition to free cyanide, it recovers some weak acid dissociable metal cyanide complexes that may or may not actually release free cyanide in the environment.

5.2.7 Weak Acid Dissociable (WAD) Cyanide—An operationally defined group of cyanide species that undergo dissociation and liberate free cyanide when refluxed under weakly acidic conditions (pH 4.5-6). Weak acid dissociable cyanide is determined analytically through weak acid distillation and analysis of liberated free cyanide (8, 10). Similar to cyanides amenable to chlorination, weak acid dissociable cyanide also provides a conservative estimate of toxicity as it recovers both free cyanide and weak acid dissociable metal cyanide complexes. This term should not be confused with the term “weak and dissociable cyanide” in Note 2.

5.2.8 Available Cyanide—A class of cyanide species that are operationally defined by their dissociation and release of free

cyanide under the action of ligand-exchange reagents. Such species are thought to be potentially bioavailable in the environment. Available cyanide is determined analytically by ligand exchange pretreatment and flow injection analysis of liberated free cyanide (13). In water, available cyanide includes free cyanide and the metal cyanide complexes of zinc, copper, cadmium, mercury, nickel and silver. As such, available cyanide is considered to provide a conservative estimate of cyanide toxicity.

NOTE 2—Available cyanide is sometimes referred to as “weak and dissociable cyanide.”

5.2.9 Organic Nitrogen—Cyanide species are included in the determination of organic nitrogen by the Kjeldahl distillation method in Test Methods D3590. The total nitrogen is determined, then ammonia-nitrogen is subtracted to calculate organic nitrogen.

NOTE 3—Test Methods D3590 digests organic nitrogen to ammonium ion and the ammonium ion combined with original ammonium present in the samples is distilled and determined as ammonia. Subtraction of ammonia in the undigested sample as determined by Test Methods D1426 or equivalent estimates the organic nitrogen present in the sample.

6. Keywords

6.1 analysis; cyanide; cyanides; environment; free cyanide; metal cyanide complex; total cyanide

APPENDIX

(Nonmandatory Information)

X1. OTHER INFORMATION

X1.1 Because of the difference in chemical stability among the various cyanide species, an environmental regulatory distinction may be made between strong metal cyanide complexes and weak acid dissociable metal cyanide complexes since only the latter can potentially release free cyanide under normal ambient environmental conditions. As such, compliance monitoring for free and dissociable cyanide is sometimes performed rather than total cyanide. Several different analytical methods have been developed over the years to recover weak acid dissociable metal cyanide complex species and free cyanide. These include the test methods: (1) cyanides amenable to chlorination, (2) weak acid dissociable cyanide, and (3) available cyanide by ligand exchange, flow injection, amperometry. Although these methods differ significantly in nature, they each were developed to recover the weak acid dissociable metal cyanide complexes and free cyanide. A brief description of each of the test methods follows.

X1.2 *Cyanides Amenable to Chlorination*—In this test method, two sample portions are analyzed. One sample is analyzed for total cyanide. The second sample portion is maintained at alkaline pH and treated with calcium hypochlorite at room temperature for a period of one hour. During this time, the weak acid dissociable metal cyanide complexes are dissociated and the free cyanide thus produced or that which was already present in the sample, or both, is destroyed via chemical oxidation to form cyanate. Following the treatment, the remaining hypochlorite is destroyed by the addition of a reductant. After chlorine removal, the sample is analyzed for total cyanide. Because strong acid dissociable metal cyanide complexes are not generally subject to chlorine oxidation, any total cyanide detected in the hypochlorite-treated sample will be due solely to the presence of strong acid dissociable metal cyanide complex species. Thus, the cyanides amenable to chlorination, which generally includes weakly complexed cyanides and free cyanide, is determined by computing the difference in concentration between the total cyanide determined in the untreated sample and that which was determined in the treated sample. The cyanides amenable to chlorination method is subject to many method interferences and can often produce results that are biased high or low depending on the sample matrix. This method is published and approved by both EPA and ASTM for regulatory reporting.

X1.3 *Weak Acid Dissociable Cyanide*—In this procedure, the pH of a sample is adjusted and maintained at 4.5 using a sodium acetate buffer. Zinc acetate is added to the sample to precipitate strong metal cyanide complexes. The sample is then refluxed for a one hour period. Under such weakly acidic conditions, the weak acid dissociable metal cyanide complex species are dissociated, releasing free cyanide. The free cyanide thus produced as well as any free cyanide already present in the sample is converted to gaseous HCN and captured as

CN⁻ in an alkaline absorption solution. The alkaline absorption solution is analyzed for cyanide to determine the weak acid dissociable cyanide. The weak acid dissociable method is published in Standard Methods and published and approved by ASTM.

X1.4 *Available Cyanide by Ligand Exchange, Flow Injection, Amperometry*—The available cyanide method was developed as a more accurate and precise alternative to the cyanides amenable to chlorination procedure. In this method, a sample is pretreated with ligand exchange reagents that liberate free cyanide from the weak acid dissociable metal cyanide complexes of zinc, copper, cadmium, mercury, nickel and silver. HCl in the reagent stream recovers completely cyanide from all above mentioned metal ions except for Hg and Ni; hence ligand exchange reagents (LERs) are needed only for the latter two species. Following treatment, the sample is injected into a flow injection analyzer where it is acidified to convert the free cyanide to HCN. The gaseous HCN thus produced is separated from the sample by passing through a gas permeable membrane. Following separation, the HCN is captured as CN⁻ in an alkaline solution and determined amperometrically. Because of the sensitivity of amperometric detection, the available cyanide method generally has lower detection limits than either cyanides amenable to chlorination or weak acid dissociable cyanide. Contrary to the distillation-based methods, the combination of room temperature ligand exchange induced release of free cyanide ion from the corresponding metal cyanide complexes, and the gas-diffusion separation step prior to amperometric quantification of cyanide renders this method nearly specific towards the analyte. The available cyanide method (EPA Method OIA-1677) is approved by the EPA Office of Water for permitting and regulatory purposes.

X1.4.1 Although the cyanides amenable to chlorination, weak acid dissociable cyanide and available cyanide methods are each intended to recover weak acid dissociable metal cyanide complexes and free cyanide, the difference in chemical nature of the test methods often leads to producing inconsistent or incomparable results, or both. In certain cases it is possible to verify the accuracy of any of these methods by determining the concentration of strong metal cyanide complexes that are present in the sample. Then, from a mass balance approach, the results may be compared to the total cyanide where the sum of the weak acid dissociable metal cyanide complexes and free cyanide determined by any of the above methods plus the strong metal cyanide complexes should equal the total cyanide.

NOTE X1.1—The mass balance approach is applicable for most industrial process waters. However, for waters that contain the metal cyanide complexes of gold, platinum, palladium or cobalt, the total cyanide analytical procedure may not yield quantitative recovery (see 5.2.3). In such cases, the mass balance approach will not be valid.

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- (12) 40 CFR Part 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants.
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SUMMARY OF CHANGES

Committee D19 has identified the location of selected changes to this standard since the last issue (D6696 – 10) that may impact the use of this standard. (Approved Jan. 1, 2014.)

(1) Revised **1.1** and **5.2.7**.

(2) Added **5.2.9** and **Note 3**.

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