



## Standard Guide for Understanding Cyanide Species<sup>1</sup>

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### 1. Scope

1.1 This guide defines standard terminology used for the classification of the 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.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1129 Terminology Relating to Water<sup>2</sup>

### 3. Terminology

3.1 *Definitions*—For a definition of terms used in this guide, refer to Terminology D 1129.

### 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 from which to discuss and reference 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*—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

relatively 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 either molecular hydrogen cyanide (HCN) or ionic cyanide ( $CN^-$ ). Hydrogen cyanide is a colorless, poisonous gas having an odor of bitter almonds (mp =  $-13.4^\circ C$ , bp =  $25.6^\circ C$ ). It is readily soluble in water partitioning itself as either HCN or  $CN^-$  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.

5.1.3 *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 dissociate in water to produce free cyanide and a cation according to the following reaction:



where:

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

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

5.1.4 *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 relatively stable and require moderate to highly acidic conditions in order to dissociate and form free cyanide. The dissociation reaction occurs as follows:



where:

M = transition metal cation,

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

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

Based on their stability, metal cyanide complexes are divided into two categories: 1) “weak metal cyanide complexes” and 2) “strong metal cyanide complexes”.

5.1.4.1 *Weak Metal Cyanide Complex*—A cyanide complex that dissociates under mildly acidic conditions ( $\text{pH} = 3\text{--}6$ ) and in dilute solutions, forming free cyanide. Because of their ability to dissociate under slightly acidic to nearly neutral, ambient conditions, the weak metal cyanide complexes are often regulated along with free cyanide in wastewater discharges. Several weak metal cyanide complexes are presented in Table 1. A weak metal cyanide complex is also sometimes referred to as a “weakly complexed cyanide” or “dissociable cyanide”.

5.1.4.2 *Strong Metal Cyanide Complex*—An extremely stable metal cyanide complex that requires strongly acidic conditions ( $\text{pH} < 2$ ) 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 and ferricyanide. In addition to these, other examples of strong metal cyanide complexes are presented in Table 2.

5.1.5 *Metal-Metal Cyanide Complex Salts*—Neutral compounds comprised of one or more metal cations and an anionic cyanide complex. The metal cations serve to 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”.

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



**TABLE 1 Selected Weak Metal Cyanide Complexes (2)**

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

<sup>A</sup>  $\text{Hg}(\text{CN})_2$  is actually a neutral species and therefore more correctly identified as a metal cyanide compound rather than a metal cyanide complex.

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

Cyanide Complex	Stability Constant (log K at 25°C)
$[\text{Fe}(\text{CN})_6]^{4-}$	35.4
$[\text{Au}(\text{CN})_2]^-$	37 <sup>A</sup>
$[\text{Hg}(\text{CN})_4]^{2-}$	39.0
$[\text{Fe}(\text{CN})_6]^{3-}$	43.6
$[\text{Co}(\text{CN})_6]^{4-}$	64 <sup>A</sup>

<sup>A</sup> This stability constant is considered to be an estimate.

where:

$A$  = alkali metal atom or ammonium ion,

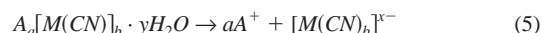
$M$  = transition metal atom,

$a$  = number of alkali metal atoms,

$b$  = number of cyanide groups, and

$y$  = number of waters of hydrate.

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



where:

$A$  = alkali metal atom,

$M$  = transition metal atom,

$a$  = number of alkali metal atoms,

$b$  = number of cyanide groups,

$x$  = ionic charge of the transition metal complex, and

$y$  = number of waters of hydrate.

5.1.5.2 *Alkaline Earth Metal-Metal Cyanide Complex Salts*—Structurally and chemically very similar to alkali metal-metal cyanide complex salts, these compounds contain an alkaline earth metal cation in place of an alkali metal cation (See 5.1.5.1).

5.1.5.3 *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:

$M$  = transition metal cation,

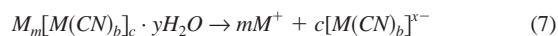
$m$  = number of transition metal cations,

$b$  = number of cyanide groups,

$c$  = number of cyanide complexes, and

$y$  = number of waters of hydrate.

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, dissociating according to the following reaction:



where:

$M$  = transition metal cation,

$m$  = number of transition metal cations,

$b$  = number of cyanide groups,

$c$  = number of cyanide complexes, and

$y$  = number of waters of hydrate.

An example of a transition metal-metal cyanide complex salt is the ferric ferrocyanide species known as prussian blue:  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ .

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 ( $\text{CH}_3\text{CN}$ ) or cyanobenzene ( $\text{C}_6\text{H}_5\text{CN}$ ). 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 radiation and exposure to strong acid followed by analysis of liberated free cyanide (7-9). In water, total cyanide includes the following dissolved species: free cyanide, weak metal cyanide complexes and strong metal cyanide complexes. However, it should be noted that some of the strong metal cyanide complexes, such as those of gold, cobalt and platinum, may 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 release free cyanide under the conditions of the analysis.

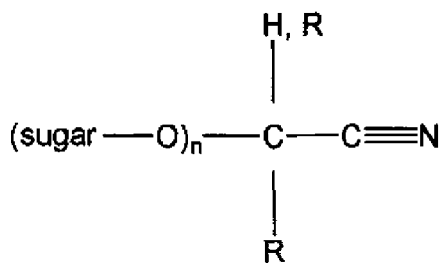


FIG. 1 Cyanogenic Glycoside General Structure

5.2.4 *Cyanides*—This term as used by the U.S. Environmental Protection Agency, describes the group of cyanide species that are dissociable in water and therefore relatively toxic in the environment (10-12). In this context, cyanides thus comprise weakly complexed cyanide species and simple cyanide species that dissociate to form free cyanide in water.

5.2.5 *Diffusible Cyanide*—The form of cyanide that is operationally defined as being capable of diffusing as HCN gas at room temperature and at a pH of 6. Diffusible cyanide is recovered and determined using microdiffusion analysis (9). In water, this form of cyanide generally includes dissolved free cyanide. Because of this, diffusible cyanide may provide a relatively accurate estimate of toxicity.

5.2.6 *Cyanides Amenable to Chlorination (CATC)*—A class of cyanide species that are operationally defined as capable of undergoing dissociation and oxidation when exposed to chlorine under alkaline conditions. These species are determined analytically by computing the difference in total cyanide of a sample treated with chlorine and an untreated sample (7-9). In water, this group of cyanide species generally includes free cyanide and the weak metal cyanide complexes. Cyanides amenable to chlorination provides a conservative estimate of toxicity because, in addition to free cyanide, it recovers some weak 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 (7, 9). 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 metal cyanide complexes.

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 toxicity.

6. Keywords

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

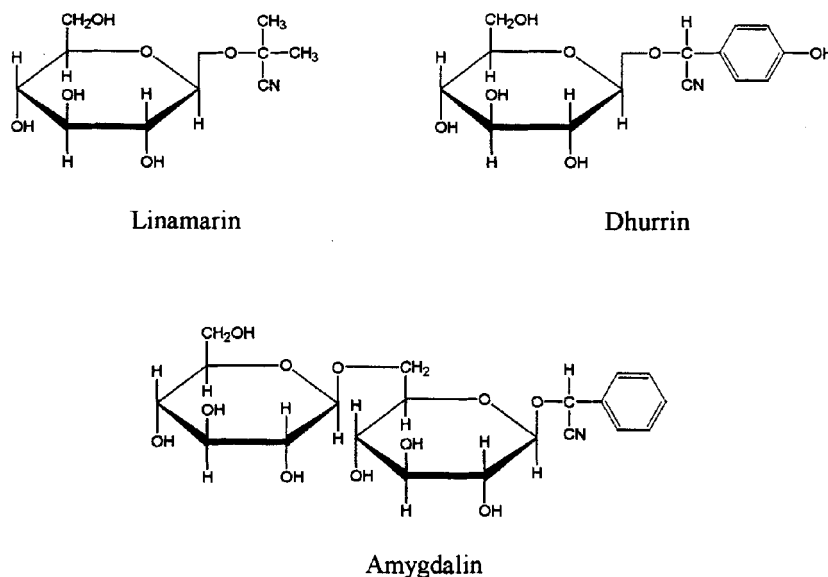


FIG. 2 Examples of Cyanogenic Glycosides

## APPENDIX

### (Nonmandatory Information)

#### X1.

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 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 often performed rather than total cyanide. Several different analytical methods have been developed over the years to recover weak 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 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 chlorine for a period of one hour. During this time, the weak metal cyanide complexes are dissociated and the free cyanide thus produced and/or that which was already present in the sample is destroyed via chemical oxidation to form cyanate. Following the treatment, the remaining chlorine is destroyed by the addition of a reductant. After chlorine removal, the sample is

analyzed for total cyanide. Because strong metal cyanide complexes are not generally subject to chlorine oxidation, any total cyanide detected in the chlorine treated sample will be due solely to the presence of strong 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, a sample is adjusted and maintained at a pH of 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 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<sup>-</sup> 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 preferentially liberate free cyanide from the weak metal cyanide complexes of zinc, copper, cadmium, mercury, nickel and silver. Following treatment, the sample is injected into a flow injection analyzer where it is acidified with 0.1 N HCl 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<sup>-</sup> 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 cy-

nides amenable to chlorination or weak acid dissociable cyanide. The available cyanide method is approved by the EPA Office of Water for regulatory reporting.

X1.4.1 Although the cyanides amenable to chlorination, weak acid dissociable cyanide and available cyanide methods are each intended to recover weak metal cyanide complexes and free cyanide, the difference in chemical nature of the test methods often leads to their producing inconsistent, incompatible results. One means of verifying the accuracy of any of these methods is to determine 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 metal cyanide complexes and free cyanide determined by any of the above methods plus the strong metal cyanide complexes should equal the total cyanide.

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