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Standard Guide for Understanding Cyanide Species[1]

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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[2]

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°C, bp = 25.6°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:

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

where:

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

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

5.1.4 *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:

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

where:

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

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

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

where:

M = transition metal cation,
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".

[1] This guide is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Organic Constituents in Water.
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[2] *Annual Book of ASTM Standards*, Vol 11.01.

5.1.4.1 *Weak 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 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 (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:

$$A_a[M(CN)]_b \cdot yH_2O \tag{4}$$

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:

$$A_a[M(CN)]_b \cdot yH_2O \rightarrow aA^+ + [M(CN)_b]^{x-} \tag{5}$$

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.

TABLE 1 Selected Weak Metal Cyanide Complexes (2)

Metal Cyanide Complex	Stability Constant (log K at 25°C)
$[Cd(CN)_4]^{2-}$	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
$Hg(CN)_2$[A]	32.8

[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.

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

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

[A] This stability constant is considered to be an estimate.

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:

$$M_m[M(CN)_b]_c \cdot yH_2O \tag{6}$$

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:

$$M_m[M(CN)_b]_c \cdot yH_2O \rightarrow mM^+ + c[M(CN)_b]^{x-} \tag{7}$$

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: $Fe_4[Fe(CN)_6]_3$.

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