

# Chemistry 101: the many faces of cyanide



28 Ni nickel 58.69	29 Cu copper 63.55	30 Zn zinc 65.39	31 Ga gallium 69.72	32 Ge germanium 72.58	33 As arsenic 74.92
46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8
78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0



Cyanide comes in many “flavours”, so to speak—not all of them palatable. This infamous compound has been linked to the deaths of Adolf Hitler and Eva Braun; was the toxin served up in the very tragic Jonestown massacre; and has even been the speculated culprit in the death of Rasputin, the Russian “wizard” (and you thought chemistry was boring!).

In the mining industry, cyanide frequently plays a key role in extracting gold from low-grade ore (i.e., in concentrations typical of most viable gold deposits). Gold is a noble metal (recall high school chemistry?) and doesn’t dissolve in water; however, a neat trick discovered by Carl Scheele in 1783 pointed to the fact that gold will readily dissolve in aqueous solutions of cyanide. Cyanide reacts with gold to form coordination complexes which are water-soluble. The Scottish further refined this process in 1887 and the MacArthur-Forrest Process was developed, which is the basis for modern-day gold extraction. The method uses solutions of cyanide, in

the presence of oxygen, to extract/leach gold from ore. From there, gold can be recovered from solution in a variety of ways (carbon-trapping, resin-trapping, electro-winning, etc.).

From a chemical perspective, cyanide compounds are pretty straightforward: cyanide refers to any chemical compound that contains the CN group, also known as the cyano group, which consists of a carbon atom triple-bonded to a nitrogen atom. There are numerous cyanide compounds. Inorganic cyanides are normally salts where the cyanide is typically the CN<sup>-</sup> anion. In many cases, similar to the gold-soluble compounds, coordination compounds are formed where the cyanide binds with the metal atom allowing it to be soluble. Organic cyanide compounds often have the cyano group bonded to an alkyl residue.

From an environmental and toxicological perspective, however, certain forms of cyanide can have extreme toxic effects and are therefore compounds of interest in

most environmental programs. Cyanide is generally classified in the following forms: Free Cyanide (FCN), Weak Acid Dissociable Cyanide (WAD), and Total Cyanide (TCN).

## GENERAL CYANIDE CLASSIFICATION

### 1. Free Cyanide (FCN):

This refers to the cyanide anion (CN<sup>-</sup>) which, when bound to hydrogen, is a clear and extremely poisonous volatile liquid. The proportions of HCN and CN<sup>-</sup> in solution are determined by their equilibrium equation and are affected by pH. Free cyanide appears in the Provincial Water Quality Objectives at a limit of five µg/L. It is also the cyanide compound of interest in the Ontario Drinking Water Standard at a Maximum Allowable Concentration of 0.2 mg/L.

### 2. WAD (Weak Acid Dissociable) Cyanide:

In terms of environmental applications, this is the most significant form of cyanide as it is toxicologically significant to eco-

logical systems. Why? WAD cyanide refers to those cyanide species liberated at a moderate pH (around 4.5)—conditions that are very likely to occur in natural or biological systems. WAD cyanide includes free cyanides, simple cyanides, and weak acid dissociable metalocyanides such as zinc- and cadmium-cyanide complexes.

### 3. Total Cyanide (TCN):

TCN cyanide refers to the sum of all forms of cyanides, including the free, non-

toxic and stable-iron cyanides. These cyanides become liberated from their complexes when hit with a strong acid.

To a much lesser degree, environmental investigations may also consider cyanate (CNO) and thiocyanate (CNS). However, these compounds are much less toxic than some of the cyanide compounds and consequently are not as commonly monitored in site or process assessments. Cyanate and thiocyanate are often measured when levels of WAD and TCN cyanide appear elevated.

### LABORATORY ANALYSIS OF CYANIDE: BEST PRACTICES

Analytical challenges associated with the measurement of cyanide include the fact that cyanide frequently complexes with metals and this can cause significant data interferences, particularly with sulfur-bearing compounds. Traditionally, analytical methods sought to remove all interferences by increasing the pH and distilling the sample prior to analyzing for WAD and TCN cyanide as a means to reduce this interference. However, distillation itself can create new analytical challenges and the U.S. Environmental Protection Agency (EPA) recently acknowledged that if sulphite or thiosulphite are present, the heat applied during distillation can actually enhance the interferences. Furthermore, distillation produces false positives in samples containing thiocyanate and nitrate, whereby thiocyanate causes a positive bias when nitrate is present and a negative bias when nitrate is absent.


In light of this, Testmark Laboratories has conducted several bench-level studies in this regard and is adopting a U.S. EPA-approved analytical method which uses ligand exchange instead of distillation. Results are found to be less fraught with interferences and are more compatible with the chemistry apparent in water from mining operations.

Given the different states of cyanide, the general rule for data is to expect

$$\text{Free CN} < \text{WAD CN} < \text{TCN}$$

Keep in mind, nevertheless, that all data has standard allowable error associated with it and therefore slight deviations from the above are expected at times. Errors associated with sampling can also greatly affect data quality.


Best practices for sampling cyanide compounds indicate that samples should be kept refrigerated and in the dark, as photolysis of iron-cyanide complexes can produce free cyanide in samples after they are taken. Preservation is also critical, with best practice being to immediately preserve with sodium hydroxide. The hold time for cyanide without preservation is extremely short—24 hours. The preserved hold time under MISA is seven days. ∞



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