



FAQ: Cyanide

Background

Cyanide is a chemical compound consisting of one carbon atom triple bonded to a nitrogen atom (figure below). Cyanide is well known because it is highly toxic to mammals, and even more so to aquatic life. Cyanide refers to all of the CN⁻ groups on cyanide compounds that can be determined as the cyanide ion.



Over a range in pH of 9.3 - 9.5, CN⁻ and HCN are in equilibrium in solution (i.e. equal amounts of each are present). At a pH of 11, over 99% of the cyanide remains in solution as CN⁻, while at pH 7, over 99% of the cyanide will exist as HCN. HCN predominates in natural waters due to the pKa of the complexes and the pH of natural waters.

Although HCN is highly soluble in water, its solubility decreases with increased temperature and under highly saline conditions. Both HCN gas and liquid are colorless and have the odor of bitter almonds, although not all individuals can detect the odor.

Cyanides are classified as simple or complex cyanides:

Simple cyanides are represented by the general form A(CN)_x where A is an alkali (sodium, potassium or ammonium) or a metal (such as copper or zinc), and x (the valence of A) is the number of CN groups.

- Simple alkali cyanides dissociate easily in aqueous solutions.

- Zinc and cadmium complexes dissociate almost completely and are toxic to fish at ordinary pH. Nickel copper and silver cyanides are more stable and thus have a lesser degree of dissociation.

Complex cyanides are represented by the general form A_yM(CN)_x Where A is the number of alkali present y times, M is the heavy metal and x is the number of CN- groups. X equals the valence of A taken y times plus the valence of M.



- Pt and Au form very stable complexes which are only partially dissociated under strong acid conditions, and minimally dissociated under environmental conditions.
- Iron cyanides are photolytic, forms HCN
- Ni, Pb, Cd, Hg cyanides are dissociable under strong acid conditions.
- Toxicity to fish of waters containing complex cyanides is due to dissociation of the complex molecule to HCN.
- Degree of dissociation increases with decreased concentration and decreased pH; inversely related to the highly variable stability of the complexes.

Sources and uses

Cyanide is not typically present in natural waters though cyanide is produced naturally in the environment by various bacteria, algae, fungi and numerous species of plants. Its presence in water normally indicates industrial contamination. While industrial sources do pre-treat, cyanide may still be found in effluent. Cyanide may be present in free form, or part of strong or weak complexes with other species. In manufacturing, cyanide is used to make paper, textiles, and plastics. It is present in the chemicals used to develop photographs. Cyanide salts are used in metallurgy for electroplating, metal cleaning, and removing gold from its ore and from water used in plating; about 1/10th of the cyanide used each year is used for mining.

Cyanide is used in other industrial processes such as manufacture of adhesives, computer electronics, fire retardants, cosmetics, dyes, nylon, paints, pharmaceuticals, rocket propellant and the production of salts. Cyanide gas is used to exterminate pests and vermin in ships and buildings. If accidentally swallowed, chemicals found in acetonitrile-based products that are used to remove artificial nails can produce cyanide when metabolized by the body.

Cyanide is also released from natural substances in some foods and in certain plants such as cassava, lima beans and almonds. Pits and seeds of common fruits, such as apricots, apples, and peaches, may have substantial amounts of chemicals which are metabolized to cyanide (Cyanogenic compounds, also known as cyanoglycosides). The edible parts of these plants contain much lower amounts of these chemicals. Cyanide is also found in cigarette smoke as well as in the combustion products of synthetic materials such as plastics.



Toxicity:

Cyanide has the highest toxicity to aquatic life as HCN. CN⁻ is less toxic but because pH in natural waters is lower than the pKa for HCN, it accounts for only a small percentage of free cyanides. HCN is also acutely toxic to humans. Liquid or gaseous hydrogen cyanide and alkali salts of cyanide can enter the body through inhalation, ingestion or absorption through the eyes and skin. The rate of skin absorption is enhanced when the skin is cut, abraded or moist; inhaled salts of cyanide are readily dissolved and absorbed upon contact with moist mucous membranes.

Cyanide has a high affinity for certain sulfur compounds (sulfanes for example, which contain two covalently bonded but unequally charged sulfur atoms) and for certain metallic complexes, particularly those containing cobalt and the trivalent form of iron (Fe³⁺). The cyanide ion can rapidly combine with iron in cytochrome a3 (a component of the cytochrome aa3 or cytochrome oxidase complex in mitochondria) to inhibit this enzyme, thus preventing intracellular oxygen utilization. The cell then utilizes anaerobic metabolism, creating excess lactic acid and a metabolic acidosis condition. Cyanide also has a high affinity for the ferric iron of methemoglobin.

Fish and aquatic invertebrates are very sensitive to cyanide exposure. 5.0 to 7.2 ug/L (ppb) of free cyanide causes adverse effects in many species of fish. Over the range of 20 - 76 ug/L, free cyanide is fatal to many species, and concentrations above 200 ug/L are deadly to almost all species of fish. Invertebrates experience adverse nonlethal effects over the range of 18 - 43 ug/L of free cyanide, and 30 - 100 ug/L is fatal.

Treatment of Effluent waters for cyanide:

The traditional method for treatment for cyanide compounds is alkaline chlorination.

- Relatively fast
- Treatment depends on the dissociation constant which also determines toxicity; time and pH factor in as well.
- Metal cyanides which don't dissociate readily require a large Cl excess and more time.
- Iron cyanides do not dissociate to any degree and are therefore not amenable to chlorination.
- Correlation exists between refractory properties in their resistance to chlorination and lack of toxicity.

The first reaction step is as follows:

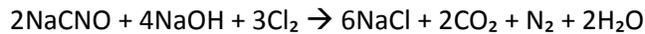


The first reaction product is cyanogen chloride (CNCl). This is a highly toxic gas whose toxicity may exceed that of HCN. At alkaline pH CNCl hydrolyzes to cyanate CNO^- , which has a much more limited toxicity:



The breakdown of CNCl is pH and time dependent. Example: at pH 9 with no excess Chlorine, CNCl can persist 24 hrs.

CNO^- can be oxidized further with Cl at ~neutral pH to CO_2 and N_2 :



Because iron cyanides do not dissociate to any degree and are therefore not affected by alkaline chlorination, it is necessary to distinguish between these and those cyanides that are amenable to chlorination. Iron cyanides are instead subject to photodecomposition. Rapid and extensive photolysis results in production of toxic HCN. Photodecomposition is dependent on exposure to UV; it is slower in dark, turbid waters and faster closer to the surface and in clean waters.

Regulatory distinction can be made between cyanides complexed with iron and those bound in less stable complexes, as well as complexed vs free (HCN).

Types of cyanides that can be determined are:

- Total cyanide
- Available cyanide
- Cyanides amenable to chlorination
- Weak acid dissociable cyanides (WAD)
- Free cyanide
- Cyanogen Chloride
- Cyanates

Total cyanide (Strong acid dissociable, or SAD): total cyanide measures almost all nondissociable cyanides, cyanides bound in complexes that are readily dissociable and complexes of intermediate



stability. Strong metal complexes including ferro-cyanide, ferri-cyanide, and those from gold and platinum are included. Total cyanide does not detect cyanate (CNO-) and thiocyanate (SCN-).

Available: Available cyanide is a fairly recent regulatory distinction. This method utilizes a ligand exchange reaction that dissociates only zinc, copper, cadmium, nickel, mercury and silver complexes. It does not dissociate gold, platinum or other strongly bound complexes that will only dissociate minimally in normal waters and are not considered toxic. This method offers greater specificity than the CATC test in matrices that are subject to interferences. It also does not require a heated distillation step; dissociation of the complexes using ligand exchange takes only a few minutes. Distillation methods take at least 30 minutes for dissociation to complete. Mining and plating facilities that discharge higher levels of minimally dissociable cyanides often use this method.

Cyanides amenable to chlorination (CATC): measures free cyanide and complex cyanides that are destroyed by chlorination at pH 11 where free chlorine is maintained for an hour. The test will include salts of alkali and alkaline earth metals plus Zn, Cd and Cu. Nickel, iron, cobalt and gold are not included. At total cyanide test is initially performed on an unchlorinated sample. Another sample is then run-this one chlorinated. Total cyanide-chlorinated sample cyanide result = cyanide amenable to chlorination.

Weak acid dissociable (WAD): Includes cyanides that are dissociated at a pH of 4.5. This includes CN and HCN and the majority of other complexes with low dissociation constants, such as Cu, Cd, Ni, Zn, Ag and Hg. Elimination of iron cyanides is ensured by chemical precipitation and avoidance of UV. Procedure frees HCN from dissociable complexes.

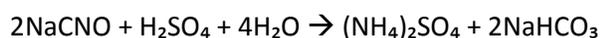
WAD and CATC are very similar tests, but there are some differences. Organic chemicals in some industrial effluents (pulp and paper, steel and petroleum refining) can oxidize or form breakdown products during chlorination, acting as an interference and resulting in higher chlorinated results than total cyanide results (negative CATC value). Since WAD cyanide does not depend on a chlorinated sample, this interference is not present.

Free cyanide: HCN and CN⁻ are the only species determined in this test. The USEPA sites amperometric determination with gas diffusion under pH conditions that are similar to the sample water. If no gas diffusion is done, results will include SCN⁻. Care must be taken to not alter the stability of weaker cyanide complexes. Interferences due to high concentrations of more stable cyanide complexes or other cyanide forms must be eliminated or tested for and allowed for in the result.

Cyanogen chloride (CNCl) : Cyanogen chloride is the highly toxic product of the first step of chlorination treatment for cyanide. Cyanogen chloride is a gas with limited solubility. Because of this, samples cannot be preserved and must be spot tested.



Cyanate: Cyanate (CNO⁻) is a product of the second step in the chlorination reaction. CNCl hydrolyzes to CNO⁻ in alkaline conditions, and cyanate is then oxidized at neutral pH with chlorine to form CO₂ and N₂. However, cyanate can also be hydrolyzed to ammonium under acidic conditions (see reaction below). The ammonia concentration is determined before and after acidification of the sample. The difference between the two measurements is the ammonia derived from cyanate.



Thiocyanate (SCN) is analogous to cyanate except the oxygen molecule is replaced by sulfur. It is not very toxic to aquatic life but forms toxic CNCl upon chlorination. In situations where chlorination is anticipated, it can be helpful to know thiocyanate concentration as well. Thiocyanate can be easily determined by combining the sample with ferric iron (Fe³⁺). At an acidic pH, this complex forms an intense red complex that can be measured colorimetrically.

Distillation:

Distillation is a critical part of most cyanide determination. It not only mitigates many possible interferences but also releases cyanide species as HCN, which is then collected and analyzed. The pH conditions of the distillation determine the species that are converted to HCN during distillation. Total cyanide also requires the addition of UV to release iron and cobalt cyanide complexes that are not dissociated through the distillation process.

Total Cyanide distillation: 1.0 M NaOH is used as an acceptor (trapping) solution. Sulfamic acid, sulfuric acid and magnesium chloride are added to the sample. The sample is then refluxed in a distillation apparatus for at least one hour. The acceptor solution containing the distilled cyanide is diluted and analyzed. This distillation is also used in determination of amenable cyanides (CATC).

WAD cyanide distillation: This distillation is carried out at a pH of 4.5-6.0. Sulfamic acid is not added, and acetate buffer and zinc acetate are added in place of sulfuric acid and magnesium chloride. Methyl red is used as a pH indicator. Acetic acid is used for pH adjustment. 0.25 M NaOH is used as a trapping solution.

Methods of detection:

These methods can be used to determine any form of cyanide. The pretreatment (or lack thereof) of the sample will determine which species of cyanide are included in the test result.



Titrimetric determination: The alkaline distillate from above is titrated with silver nitrate to form soluble silver cyanide. Once all of the available cyanide has been complexed and a small excess of silver has been added, the excess is detected by the *p*-dimethylaminobenzalrhodanine indicator, which turns from a yellow to salmon color.

Colorimetric determination:

Pyridine-barbituric acid reaction: Cyanide in the distillate is converted to CNCl using Chloramine-T at a pH <8. The cyanogen chloride then forms a red-blue color upon addition of a pyridine-barbituric acid reagent. Maximum absorbance is between 575 and 582 nm.

Pyridine-pyrazolone reaction (Hach): Cyanide is converted to CNCl using CyaniVer3 reagent, which contains chlorine. Pyridine is then added through the CyaniVer4 reagent, forming an intermediate nitrile. The nitrile is hydrolyzed to glutacanaldehyde which reacts with pyrazalone from the CyaniVer5 reagent to form a blue color which is directly proportional to the amount of cyanide in the sample.

Cyanide Selective Electrode: Potentiometric determination uses a cyanide sensitive electrode in combination with a double junction reference electrode and a suitable pH meter.

Interferences:

Oxidizing agents such as chlorine will decompose most cyanides. Use KI-starch paper and acetate buffer to test for the presence of oxidizers.

Sulfide will distill over with cyanide and will form SCN rapidly. You can test for sulfide by placing a drop of sample on lead acetate paper that has been moistened with acetic acid buffer solution. Samples containing sulfide should be treated with lead acetate or lead carbonate until the sample no longer darkens the lead acetate paper.

Fatty acids can interfere with end-point detection in alkaline titration. These should be removed by extraction. Extraction should be formed carefully and quickly to prevent excess loss of cyanide.

Carbonate in high concentrations can interfere with distillation procedure by causing the violent off gassing of carbon dioxide and foaming when adding acid. Preserve these types of samples with calcium hydroxide.

Aldehydes convert cyanide to cyanohydrin, which forms nitrile under distillation conditions. Samples containing aldehydes can be determined using direct titration without distillation; only non-complexed



cyanides are thus included. Aldehyde interference can be minimized through the addition of ethylenediamine solution to the sample to reduce cyanohydrin to cyanide.

Glucose and other sugars at the pH of preservation lead to cyanohydrin formation by reacting cyanide with an aldose. Ethylenediamine is used to reduce cyanohydrin to cyanide (see above).

Nitrite may form HCN during distillation by reacting with organic compounds. *Nitrate* can also interfere by reducing to nitrite or by reacting with SCN.

Sulfur compounds may decompose during distillation, releasing H₂S or SO₂ which can convert cyanide to thiocyanate. Absorbed SO₂ forms Na₂SO₃ which consumes the chloramine-T added for colorimetric determination.

**Some industrial wastes are susceptible to interferences from the conversion of thiocyanate to cyanide in the presence of an oxidant such as nitrate. Ligand exchange reactions (see available cyanide) to dissociate metal-cyanide complexes can be used in these circumstances.