Cyanide

Because cyanide is toxic to humans, a maximum acceptable concentration of *0.2 mg/L (200 µg/L)* for free cyanide in drinking water has been set.

General

Cyanide refers to the –C≡N anion radical. Compounds capable of releasing cyanide may be inorganic or organic in nature. Inorganic compounds may be simple (e.g., AgCN, KCN) or complex (e.g., $A[CN]_y$, $A[M]_x[CN]_y$). Organic compounds may be glycosides or nitriles. This summary deals mainly with hydrogen cyanide (HCN), cyanogen (CN^-) and simple salts of HCN that dissociate readily to release CN^-. Free cyanide is defined as the sum of the cyanide present as either HCN or CN^-.[1]

Hydrogen cyanide is a colourless liquid with an odour characteristic of bitter almonds and a vapour pressure of 107.6 kPa at 27.2°C;[2] it is completely miscible in water.[3] Potassium cyanide, a white granular powder, and sodium cyanide, a white crystalline solid, are both readily soluble in water.[2,3]

Some commercial applications of cyanide include electroplating, extraction of ores (gold, silver), metal processing, photographic processes, production of synthetic rubber, chemical synthesis, manufacture of plastics, pesticide/rodenticide control, dehairing of hides, laboratory processes and the manufacture of dyes and pigments.[4–9]

In Canada, in 1973, the consumption of sodium cyanide, potassium cyanide and miscellaneous cyanide was reported to be approximately 268.3, 16.3 and 87.3 t/year, respectively.[10]

Occurrence

In Canada, cyanides may be released into the aquatic environment through waste effluents from the organic chemical and gold mining and milling industries, as well as from industrial processes such as gas works, coke ovens, gas scrubbing in steel plants, metal cleaning and electroplating.[11] Cyanide in the aquatic environment may also be associated with non-point sources, including runoff from the application on land and water of salt containing cyanide compounds as anti-caking agents.[4]

In all but highly alkaline waters, cyanide exists predominantly as free cyanide. Under typical conditions in natural waters (pH 6 to 8.5 and 4 to 10°C), over 90% of cyanide is in the form of molecular HCN.[12] Conversion of cyanide to a less toxic cyanate occurs at pH levels of 8.5 and above.

In general, cyanide concentrations in raw water appear to be low (i.e., <0.1 mg/L).[9] In a survey of 11 rivers in western and central Canada between 1974 and 1977, total cyanide concentrations were often as high as 30 to 60 µg/L, with peak levels related to the size of the watershed and seasonal runoff.[5] Samples collected from streams (1849 samples), lakes (361 samples) and marine waters (22 samples) in British Columbia between 1965 and 1976 had total cyanide concentrations of 10, 40 and <10 µg/L, respectively.[13] Surface water sampled across Canada contained cyanide at concentrations ranging from not detected to 9.7 µg/L (detection limit 0.5 µg/L) for the Pacific Region (1980 to 1983); <2 to 2.1 µg/L (detection limit ~2 µg/L) for the Western Region (prior to 1980); and <2 to 370 µg/L (detection limit ~2 µg/L) for the Central Region (1980 to 1983).[14] More recent (1989) surface water data available in the NAQUADAT data base showed average cyanide concentrations of 5 µg/L for Manitoba, 4 µg/L for Saskatchewan and 3 µg/L for Alberta.[15]

Maintenance of a free chlorine residual under neutral or alkaline conditions will result in very low concentrations of cyanide in finished water.[16] In 1975, raw and treated water from the Ottawa River contained cyanide at concentrations below 10 µg/L.[17] The overall averages of monthly average cyanide concentrations in samples of raw, treated and distributed water from supplies in Ontario were all below the detection limit of 1 µg/L in 1988.[18] In 1975, treated water supplies from 116 of 124 stations in Manitoba contained cyanide at concentrations below 100 µg/L, with a median value of 30 µg/L.[19] More recent (1988) data from Manitoba supply systems indicated that cyanide concentrations were below the detection limits of 10 to 20 µg/L for raw water and 1 to 10 µg/L for treated water.[20]

Cyanides are uncommon in U.S. water supplies, with concentrations usually not exceeding 10 µg/L.[6] In a U.S. survey of 969 water supplies (2595 samples), the highest cyanide concentration was 8 µg/L, and the

average concentration was 0.09 µg/L.[7,21] All but one water sample collected in the United Kingdom contained cyanide at concentrations below 50 µg/L, the exception containing 100 µg/L.[22] Data obtained from the U.S. Environmental Protection Agency STORET data base indicate that mean cyanide concentrations in most surface waters tested in the United States do not exceed 3.5 µg/L.[23]

Most foods contain traces of cyanides, including cassava, sweet potatoes, yams, maize, millet, bamboo, sugarcane, peas and beans, as well as kernel of almond, lemon, lime, apple, pear, cherry, apricot, prune and plum.[23–25] Examples of cyanide levels measured in selected foods include 0.001 to 0.45 µg/g for cereal grains and their products; 0.07 to 0.3 µg/g for soy protein products; 1 mg/g for cassava; and 0.1 to 3 mg/g for lima beans.[24] The presence of cyanide in food of plant origin has been attributed to natural production within the plants and uptake from the surrounding soil;[26] however, soil concentrations are expected to be low, as the cyanide ion is not strongly adsorbed and retained in soils,[6,27] and numerous micro-organisms are able to degrade free cyanide to carbon dioxide and ammonia.[6] As well, some cyanide residues have been detected in food treated with cyanide fumigants.[6] Although cyanides can be found in fish from contaminated waters, the cyanides readily decompose upon heating, and cooked foods contain little or no cyanide.[9]

Canadian data on cyanide levels in the atmosphere are not available; levels are probably extremely low owing to the instability of cyanide.

Canadian Exposure

Representative data suggest that Canadian drinking water has very low concentrations (<100 µg/L) of cyanide. Contamination through industrial spillage or transport accidents could result in high cyanide levels in raw water supplies. Canadian exposure to cyanide through the average diet and from the atmosphere is thought to be extremely low.

Analytical Methods and Treatment Technology

Cyanide in water is usually determined in three different forms: free cyanide, cyanide amenable to chlorination and total cyanide. Free cyanide is a measure of the cyanide present as HCN or CN^-, and total cyanide is a measure of all cyanides, including iron cyanide complexes. Methods for determining cyanide amenable to chlorination measure simple metal cyanides and most complex cyanides with the exception of iron cyanides.[4]

Drinking water can be analysed for cyanide using volumetric titration or colorimetry, with detection limits of 1 mg/L and 20 µg/L, respectively.[7] Other methods include absorption spectrophotometry, ion-selective electrodes, indirect atomic absorption spectrophotometry, fluorometry and gas chromatography, with detection limits of 0.5 µg/L, 25 µg/L, 60 µg/L (iron complex)/30 µg/L (silver cyanide), 1 µg/L and 0.2 µg/L, respectively.[4,6]

There are various methods for the removal of cyanides from water, although most apply to removal of cyanide from wastewater. Some of the processes more frequently used in drinking water treatment are destruction by chlorination, ozone oxidation, ion exchange, reverse osmosis and electrolytic decomposition (where cyanide concentrations are very high). In destruction by chlorination, probably the cheapest and most practical method, the cyanide may be either partially oxidized to cyanate or completely oxidized to carbon dioxide and nitrogen. Ozone oxidation is a relatively new technique, used when the formation of trihalomethanes must be avoided.[7,8,28]

Health Considerations

Absorption, Distribution and Excretion

Absorption of cyanide occurs across both mucous membranes and intact skin.[29] The most common inorganic cyanides are readily absorbed through the stomach and duodenum. Absorption by the gastrointestinal mucosa is dependent on the pH of the gut and the lipid solubility of the specific cyanide compound.[4]

Cyanides are rapidly distributed to all organs and tissues via the blood. The cyanide concentration is higher in red blood cells than in plasma by a factor of two or three, reflecting cyanide's tendency to bind to methaemoglobin. Cyanide may also accumulate in body cells by binding to metalloproteins or enzymes such as catalase or cytochrome c oxidase.[29] Cyanide levels in a woman who died 30 minutes after ingesting 2.5 g NaCN were highest (up to 3.2 mg% [3.2 mg/100 g]) in the stomach contents, brain and urine.[30] Two other studies found the concentration of cyanide to range from 0.2 to 2 mg% in the liver, kidneys and brain of poisoned humans.[31,32] It has been reported that small but significant levels of cyanide are present in normal, healthy human organs at concentrations of ≤0.5 mg/kg (as CN^-), owing to the breakdown of cyanogenic foods and tobacco smoke by bacterial action and vitamin B_{12}.[33]

Cyanide is rapidly detoxified in the body by conversion to the much less toxic thiocyanate (CNS) ion.[34] The major pathway for this conversion is via the intramitochondrial enzyme rhodanese, a liver enzyme that catalyses the transfer of sulphur from a donor to cyanide to form thiocyanate.[4,7]

Urine has been found to be the major route of excretion of thiocyanate. Average urinary excretion of thiocyanate normally ranges between 0.85 and 14 mg over a 24-hour period.[4] However, one case report describes a urinary excretion of 237 mg in 72 hours by a

man who ingested 3 to 5 g KCN.[35] Some cyanide is metabolized directly, and carbon dioxide is eliminated in expired air. A small amount of HCN is also eliminated in expired air.[7]

Toxic Effects

The cyanides reviewed in this document are highly lethal to humans; lethal oral doses of cyanide compounds generally range from 50 to 200 mg CN (0.7 to 2.9 mg/kg bw);[36] based on case reports of poisonings, an average fatal dose of cyanide has been estimated to be 1.52 mg/kg bw.[37] The lowest recorded lethal dose for humans is 0.56 mg/kg bw (as CN^-).[38] Death usually occurs within one hour.[1] Low exposures to cyanide are not fatal to humans with efficient detoxification systems.[9]

In a two-year chronic toxicity study in which male and female rats were fed cyanide at doses as high as 7.5 and 10.8 mg/kg bw per day, respectively, no clinical or histopathological effects of any kind were observed.[39]

Cyanide acts through the inhibition of cytochrome c oxidase in the respiratory electron transport chain of the mitochondria, impairing both oxidative metabolism and the associated process of oxidative phosphorylation.[40,41] Its outward acute effects resemble those of acute hypoxia. Interference in the oxidation process may also give rise to cardiac disturbances, seizures, unconsciousness and, ultimately, death.

Neurological disorders and thyroid abnormalities have been linked with long-term consumption of cassava, a tuberous root vegetable containing natural cyanogens.[42,43] Surveys in African communities where cassava is a staple crop show a strong correlation between cassava consumption and endemic goiter and cretinism. Dietary deficiencies, especially low intake of iodine, may contribute to these effects.[44,45]

Rationale

1. Food and drinking water are the main sources of cyanide exposure for individuals who are not occupationally exposed to the chemical. Cyanide ion is an extremely toxic and fast-acting poison; however, it can be detoxified to a certain extent in the human body.

2. Single oral doses of 50 to 200 mg cyanide have produced fatalities in humans. Daily oral doses of 2.9 to 4.7 mg cyanide are generally considered to be non-injurious to humans owing to the efficient detoxification of cyanide to thiocyanate.[46]

3. In a two-year chronic toxicity study, no clinical or histopathological effects were observed in female rats consuming as much as 10.8 mg CN^-/kg bw per day in the diet. Based on the results of this study, the maximum acceptable concentration of free cyanide in drinking water was determined to be 0.2 mg/L. Surveys of raw and finished waters indicate that levels of cyanide are usually less than 0.1 mg/L. Chlorination of water to a chlorine residual under neutral or alkaline conditions will reduce cyanide concentrations to low levels.

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