# ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA ENTRY ON CYANIDE(S) IN GENERAL

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Like a library or most large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...

No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also a major issue related to (lack of) data comparability from media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it

simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even with out updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese, and W. Basham. 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

# Cyanide(s) in General (No CAS Number) and Free Cyanide (CAS number 57-12-5)

NOTE: With the permission of Ron Eisler, Eisler's 1991 comprehensive, public domain summary on hazards of selected contaminants to plants and animals is used extensively in this document in word-for-word quotes. Each of these quotes is attributed to Eisler [517].

#### Brief Introduction:

Br.Class: General Introduction and Classification Information:

The chemical speciation of cyanides varies according to their source. Specific terms used to describe cyanide include free cyanide, cyanide ion, simple cyanides, complex cyanides, nitriles, cyanogens, and total cyanide. The most common forms of cyanide in the environment are free cyanide, metallocyanide complexes, and synthetic nitriles [517]. For a detailed description of these forms of cyanide see the Chem.Detail and Forms/Preparations/Formulations sections below.

Cyanides are used widely and extensively in the manufacture of synthetic fabrics and plastics, in electroplating baths and metal mining operations, as pesticidal agents and intermediates in agricultural chemical production, and in predator control devices [517].

Because of their highly effective lethal potency, cyanides were used for genocidal programs in Germany in World War II, in mass suicides by members of the People's Temple religious sect in Guyana, and in the substitution of medication in Tylenol capsules in drugstores in various cities in the United States. In fact, cyanides are responsible for more human deaths than any other chemicals known, owing to their deliberate use in suicide, murder, chemical warfare, genocide, and judicial execution [517].

Cyanide is a non-carcinogenic priority pollutant [446,564]. Cyanide seems not to have any direct effect on recreational uses of water other than its effect on aquatic life [375].

Designated as a hazardous substance under section 311(b)(2)(A) of the Federal Water Pollution Control Act and further regulated by the Clean Water Act Amendments of 1977 and 1978. These regulations apply to discharges of this substance. (40 CFR 116.4, 7/1/88) [366].

Toxic pollutant designated pursuant to section 307(a)(1)

of the Clean Water Act and is subject to effluent limitations. /Cyanides/ (40 CFR 401.15, 7/1/88) [366].

Total cyanides is the most often cited measurement in aqueous solutions, owing to limitations in analytical methodologies [517]. There is general agreement that total cyanide concentrations in water in most cases will overestimate the actual cyanide toxicity to aquatic organisms, and that the analytically determined HCN concentration in cyanide-polluted waters is considered to be the most reliable index of toxicity [517].

Free cyanide is the primary toxic agent in the aquatic environment. Free cyanide refers to the sum of molecular HCN and the cyanide anion (CN-), regardless of origin. In aqueous solution with pH 9.2 and lower, the majority (>90%) of the free cyanide is in the form of molecular HCN [517,754].

Many chemical forms of cyanide are present in the environment, including free cyanide, metallocyanide complexes, and synthetic organocyanides, also known as nitriles [517].

# Br.Haz: General Hazard/Toxicity Summary:

The observed toxicity to aquatic life of simple and complex cyanides was attributed almost entirely to molecular (undissociated) hydrocyanic acid (HCN) derived from ionization, dissociation, and photodecomposition of cyanide-containing compounds. The toxicity of the cyanide ion, CN-, which is a minor component of free cyanide (HCN + CN-) in waters that are not exceptionally alkaline is of little importance. The acute toxicity of stable silver cyanide and cuprocyanide complex anions is much less than that of molecular HCN, but is nevertheless important; these ions can be the principal toxicants, even in some very dilute solutions. The much lower toxicities of the ferrocyanide and ferricyanide complexions -- which are of high stability but subject to extensive and rapid photolysis, yielding free cyanide on direct exposure to sunlight -- and the nickelocyanide ion complex are not likely to be of practical importance. Toxicity to aquatic organisms of organic cyanide compounds, such as lactonitrile, is similar to that of inorganic cyanides because they usually undergo rapid hydrolysis in water to free cyanide. There is general agreement that total cyanide concentrations in water in most cases will overestimate the actual cyanide toxicity aquatic organisms, and that the analytically determined HCN concentration in cyanide-polluted waters is considered to be the most reliable index of toxicity [517].

Cyanide is readily absorbed from all routes, including skin, mucous membranes, and inhalation, although alkali salts of cyanide are toxic only when ingested [669]. Many of the metal salts of HCN (sodium cyanide, mercury cyanide, copper cyanide, etc.) are considered hazardous inorganic cyanides [480].

Numerous biological and abiotic factors are known to modify the biocidal properties of free cyanide, including water pH, temperature, and oxygen content; life stage, condition, and species assayed; previous exposure to cyanide compounds; presence of other chemicals; and initial dose tested [517].

Elevated cyanide levels are normally encountered in more than 1,000 species of food plants and forage crops, and this probably represents the greatest source of cyanide exposure and toxicosis to man and to range animals [517].

Cassava, also known as manioc, tapioca, yuca, or guacamate, is one of the very few--and, by far, the most important--food crops in which the cyanide content creates toxic problems [517].

Only free cyanide (i.e., the sum of molecular hydrogen cyanide, HCN, and the cyanide anion, CN-) is the primary toxic agent, regardless of origin [517]. The most toxic form of cyanide in water is probably hydrocyanic acid [375].

Adverse effects of cyanide on aquatic plants are unlikely at concentrations that cause acute effects to most species of freshwater and marine fishes and invertebrates [517].

Cyanide hazards to fish, wildlife, and livestock are well documented. Massive kills of freshwater fish accidental discharges of cyanide wastes are fairly common. In one case, cyanide-containing mine effluents from a Canadian tailings pond released into a nearby creek killed more than 20,000 steelhead (Oncorhynchus Many species of birds were found dead near mykiss. burrows of the black-tailed prairie dog (Cynomus ludovicianus) after the burrows had been treated with calcium cyanide to control prairie dog populations; dead birds included the burrowing owl (Athene cunicularia), the bald eagle (Haliaeetus leucocephalus), and the golden eagle (Aquila chrysaetos). An endangered California condor (Gymnogyps californianus) found dead in Kern County, California, in November 1983 had particles of a yellow fluorescent tracer in its mouth; these particles were similar to those mixed with sodium cyanide in M-44 spring-loaded ejector mechanism devices used in a U.S. Fish and Wildlife Service Animal Damage Control Program

in that vicinity, suggesting that cyanide was a possible cause of death. M-44 devices are known to have caused the death of magpies (Pica sp.), ravens and crows (Corvus spp.), wild turkeys (Meleagris gallopavo), and various unidentified species of hawks and vultures. Between 1980 and 1989, 519 mammals--mostly rodents (35%) and bats (34%) -- were found dead at cyanide-extraction, gold-mine leach ponds in California, Nevada, and Arizona; the list included coyote (Canis latrans), foxes, skunks, badger (Taxidea taxus), weasels, rabbits, deer, and beavers. Also found dead at these same leach ponds were 38 reptiles, 55 amphibians, and 6,997 birds, including many species of waterfowl and songbirds. The influence of cyanide-extraction gold-mining operations on wildlife is currently under investigation by scientists at the Patuxent Wildlife Research Center [517].

The major threat of cyanide poisoning to livestock and terrestrial mammalian wildlife is through ingestion of plants containing high levels of cyanogenic glycosides. Plants implicated in cyanide poisoning of animals include the sorghums (Johnson grass, Sorghum halepense; Sudan grass, Sorghum almum), arrowgrass (Triglochin spp.), elderberry (Sambucus spp.), wild cherry (Prunus spp.), and the pits of several common fruits, such as apple, peach, and apricot; these plants and fruit pits have the potential of releasing cyanide upon ingestion. Domestic goats (Capra spp.) died of cyanide poisoning after eating leaves and fruit of the crab apple (Malus sylvestris); the crab apple contains cyanogenic glycosides in its leaves and fruit. Cyanide poisoning of cattle (Bos spp.) by forage sorghums and various hybrid cultivars has been reported in India and elsewhere. Cattle appear to be more vulnerable to cyanide poisoning than are sheep (Ovis aries), horses (Equus cabalus), and pigs (Sus spp.). Equine sorghum cystitis ataxia is a condition observed in horses grazing Sorghum or hybrid sudan grass pastures; it is characterized by urinary incontinence, posterior incoordination, and degenerative central nervous system Grazing cyanogenic plants can induce sulfur deficiency in sheep, presumably because sulfur detoxifies the released cyanide. The increasing use of cassava and other cyanogenic plants in animal feeding portends a greater exposure to dietary cyanides [517].

Cyanide inhibits ion transport mechanisms in amphibian skin, gall bladder, and proximal renal tubules. Measurable changes in cell membrane potentials of isolated gall bladder epithelium cells, for example, were induced by NaCN in a salamander (Necturus maculosus). Cyanide-induced hyperpolarization was caused primarily by an increase in permeability of the cell membrane to potassium, which, in turn, was mediated by an elevation of intracellular calcium ion activity, attributable to

release from mitochondrial sources [517].

Most authorities now agree that in mammals: (1) cyanide has an unusually low chronic toxicity, but chronic intoxication exists and, in some cases, can be incapacitating; (2) despite the high lethality of large single doses or acute respiratory exposures to high vapor concentrations of cyanide, repeated sublethal doses seldom result in cumulative adverse effects; and (3) cyanide, in substantial but sublethal intermittent doses can be tolerated by many species for long periods, perhaps indefinitely [517].

low lethal doses of cyanide, the effects principally on cytochrome oxidase in the central nervous system. At higher doses, cardiovascular signs and changes in electrical activity of the brain are among the most consistent changes measured. Acute and subacute toxic effects of poisoning with cyanide can vary from convulsions, screaming, vomiting, and bloody frothing to less dramatic events, such as a slow, quiet onset to coma and subsequent death. In the first stage of cyanide poisoning, victims exhibit headache, vertigo, weak and rapid pulse, nausea, and vomiting. In the second stage, there are convulsions, falling, dilated pupils, clammy skin, and a weaker and more rapid pulse. In the final stage, heartbeat becomes irregular and slow, body temperature falls, there is cyanosis of lips, face, and extremities, coma, frothy bloody saliva flow from mouth, and death. If acute exposure is to a sublethal dose of cyanide, this may lead to signs of toxicity, but as detoxification proceeds these signs will become less obvious and eventually vanish, and cyanide will be excreted as thiocyanate without accumulating [517].

Cyanide is a potent and rapid-acting asphyxiant; it induces tissue anoxia through inactivation of cytochrome oxidase, causing cytotoxic hypoxia in the presence of normal hemoglobin oxygenation. Diagnosis of acute lethal cyanide poisoning is difficult because signs and symptoms are nonspecific, and numerous factors modify its biocidal properties, such as dietary deficiencies in vitamin B12, iodine, and sulfur amino acids [517].

Cyanide is a general respiratory poison—although uptake can also occur through ingestion or dermal absorption—producing reactions within seconds, and death within minutes [517]. The toxic mechanism of cyanide primarily involves the inhibition of cytochrome oxidase, the terminal oxidative enzyme of the mitochondrial electron transport chain, producing blockage of aerobic ATP synthesis [517].

No human cases of illness or death due to cyanide in

water supplies are known [517].

A comprehensive toxicological profile for cyanide, especially as it relates to human health, is available from ATSDR [755]. Due to a lack of time, important highlights from this ATSDR document have not yet been completely incorporated into this entry. EPA also has a free and informative (several page) health advisory on cyanide, available through the Office of Drinking Water, EPA, Washington, D.C. or through NTIS.

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

EPA 1996 Integrated Risk Information System (IRIS) Database Information on free cyanide, CAS number 57-12-5 [893]:

Evidence for classification as to human carcinogenicity; weight-of-evidence classification:

Classification: D; not classifiable as to human carcinogenicity [893].

BASIS: Pertinent data regarding carcinogenicity have not been located in the available literature [893].

HUMAN CARCINOGENICITY DATA: None [893].

ANIMAL CARCINOGENICITY DATA: None [893].

All available evidence suggests that cyanides are not carcinogenic [517].

**Br.Dev:** Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Cyanide, like many other chemicals, can stimulate growth of fish during exposure to low sublethal levels. This phenomenon, referred to as hormesis, is little understood and warrants additional research [517].

Low concentrations of HCN caused developmental abnormalities in embryos of Atlantic salmon after extended exposure [517].

Cyanide adversely affects fish reproduction by reducing the number of eggs spawned, and the viability of the eggs by delaying the process of secondary yolk deposition in the ovary [517].

Sperm motility in rainbow trout can be affected by HCN [517].

Reproductive impairment in adult bluegills (Lepomis macrochirus) has been reported following long-term exposure to CN. Fertilized fish eggs are usually resistant to cyanide prior to blastula formation, but delayed effects can occur, including birth defects and reduced survival of embryos and newly hatched larvae [517].

All available evidence suggests that cyanides are neither mutagenic nor teratogenic [517].

Cyanide produces chromosomal aberrations in some plants, but the mode of action is unknown [517].

In vitro studies of genotoxicity have been negative except for a marginally mutagenic response for HCN in Salmonella typhimurium strain TA100; this response was decreased in the presence of rat hepatic homogenates [893].

**Br.Fate:** Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Most authorities now agree that: (1) cyanide has low persistence in the environment and is not accumulated or stored in any mammal studied; (2) cyanide biomagnification in food webs has not been reported, possibly due to rapid detoxification of sublethal doses by most species, and death at higher doses [517].

In water, cyanides occur as free hydrocyanic acid, simple cyanides, easily degradable complex cyanides such as zinc cyanide, and sparingly decomposable complex cyanides of iron and cobalt; complex nickel and copper cyanides are intermediate between the easily decomposable sparingly degradable compounds. Cyanide has relatively low persistence in surface waters under normal conditions but may persist for extended periods in ground water. Volatilization is the dominant mechanism for removal of free cyanide from concentrated solutions and is most effective under conditions of high temperatures, high dissolved oxygen levels, and at increased concentrations of atmospheric carbon dioxide. Loss of simple cyanides from the water column is primarily through sedimentation, microbial degradation, and volatilization. Water-soluble complexes, such as ferricyanides ferrocyanides, do not release free cyanide unless exposed to ultraviolet light. Thus, sunlight may lead to cyanide formation in wastes containing iron-cyanide complexes [517].

Under natural conditions, the ratio of hydrocyanic acid

to total cyanide fluctuates frequently due to changes in pH caused by acid wastewater discharges or by photosynthetic and respiration cycles of aquatic plant life [302].

Cyanide seldom remains biologically available in soils because it is either complexed by trace metals, metabolized by various microorganisms, or lost through volatilization. Cyanide ions are not strongly adsorbed or retained on soils, and leaching into the surrounding ground water will probably occur [517].

There are no reports of cyanide biomagnification or cycling in living organisms, probably owing to its rapid detoxification. Cyanide seldom persists in surface waters and soils owing to complexation or sedimentation, microbial metabolism, and loss from volatilization. More data are needed on cyanide distribution and transformation in the atmosphere [517].

Although cyanide is ubiquitous in the environment, levels tend to be elevated in the vicinity of metal processing operations, electroplaters, gold-mining facilities, oil refineries, power plants, and solid waste combustion [517].

Analytical methods for the determination of free and bound cyanides and cyanogenic compounds in biological materials are under constant revision. Further, unless tissue samples are obtained promptly after cyanide exposure and analyzed immediately, erroneous analytical values will result [517].

## Synonyms/Substance Identification:

For the cyanide ion (CAS 57-12-5) only, the synonyms include [617]:

Cyanide Cyanide anion Cyanide ion Isocyanide

For hydrogen cyanide only, the synonyms include [365]:

ACIDE CYANHYDRIQUE (French) [365]
ACIDO CIANIDRICO (Italian) [365]
AERO LIQUID HCN [365]
BLAUSAEURE (German) [365]
BLAUWZUUR (Dutch) [365]
CARBON HYDRIDE NITRIDE (CHN) [365]
CYANWATERSTOF (Dutch) [365]
CYANWASSERSTOFF (German) [365]

CYCLON [365] CYCLONE B [365] CYJANOWODOR (Polish) [365] EVERCYN [365] FLUOHYDRIC ACID GAS [365] FORMIC ANAMMONIDE [365] FORMONITRILE [365] HCN [365] HYDROCYANIC ACID (DOT) [365] HYDROFLUORIC ACID GAS [365] HYDROGEN CYANIDE [365] HYDROGEN CYANIDE (ACGIH, OSHA) [365] NA 1051 (DOT) [365] PRUSSIC ACID [365] PRUSSIC ACID, UNSTABILIZED [365] RCRA WASTE NUMBER P063 [365] UN 1051 (DOT) [365] UN 1613 (DOT) [365] UN 1614 (DOT) [365] ZACLONDISCOIDS [365]

Associated Chemicals or Topics (Includes Transformation Products):

See also Forms/Preparations/Formulations section below.

Metabolism/Metabolites information from HSDB for hydrogen cyanide (HCN) [366]:

Larger portion /of absorbed cyanide/ ... Is converted by ... Sulfurtransferase/s/ to ... Thiocyanate ion. ... Minor metabolic pathways incl combination with cystine to form 2-imino-thiazolidine-4-carboxylic acid, oxidation to carbon dioxide & formate, & conversion to cyanocobalamin. [Goodman, L.S., and A. Gilman. (eds.) The Pharmacological Basis of Therapeutics. 5th ed. New York: Macmillan Publishing Co., Inc., 1975. 904].

The enzymatic decomposition of thiocyanate into cyanide by a thiocyanate oxidase has been found in mammals, but only in erythrocytes. [Nat'l Research Council Canada; The Effects of Cyanides on Aquatic Organisms With Emphasis Upon Fresh Water Fishes p.61 (1976) NRCC No.19246].

A very small fraction of the total cyanide is bound by hydroxocobalamin, probably less than 1 percent. [Brink NG et al; Science 112: 354 (1950) as cited in USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-14 (1980) EPA 440/5-80-037].

Because the liver contains the highest activity of rhodanese, it is possible that existing liver disease might slow the rate of cyanide metabolism. [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-14

(1980) EPA 440/5-80-037].

Cyanide is converted to products which enter metabolic pathways for one-carbon compounds and is converted to formate and to carbon dioxide. [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-14 (1980) EPA 440/5-80-037].

Hydrogen cyanide reacts with acetaldehyde followed by hydrolysis to produce lactic acid [CHEMICAL PRODUCTS SYNOPSIS: Hydrogen Cyanide, 1983].

Cyanide is conjugated with sulfur to form ion thiocyanate. ... Conjugation is catalyzed by ... Rhodanese which is widely distributed in most animal tissues ... /Liver/ particularly active. ... Rhodanese mechanism is capable of detoxicating only limited amt of cyanide, such as are formed during normal metab. /Another 3-mercaptopyruvate. The sulfur donor is enzyme, mercaptosulfur transferase is localized in cytosol./ /Cyanide/ [Parke, D. V. The Biochemistry of Foreign Compounds. Oxford: Pergamon Press, 1968. 96].

Nitroprusside releases cyanide in vivo, and cyanide toxicity is a true complication of its use. [Arnold WP et al; Anesthesiology 61 (3): 245-60 (1984)].

One of the major mechanisms for removing cyanide from the body is its enzymatic conversion, by the mitochondrial enzyme rhodanese (transsulfurase), to thiocyanate, which is relatively . [Gilman, A.G., L.S.Goodman, and A. Gilman. (eds.). Goodman and Gilman's The Pharmacological Basis of Therapeutics. 7th ed. New York: Macmillan Publishing Co., Inc., 1985. 1643].

Ruminants are more susceptible to poisoning by cyanogenic plants /srp: which release hydrogen cyanide/ than are horses & pigs ... /Cyanogenic plants/ [Clarke, M. L., D. G. Harvey and D. J. Humphreys. Veterinary Toxicology. 2nd ed. London: Bailliere Tindall, 1981. 176].

Factors that incr likelihood of HCN poisoning from ingestion of cyanogenic plants include: (1) large amt of free HCN & cyanogenic glycoside in plant, (2) rapid ingestion; (3) ingestion of a large amt of plant, & (4) ruminal ph & microflora that continue to hydrolyze glycoside /srp: to release hydrogen cyanide/. Rapid intake of plant ... Equiv to about 4 mg HCN/kg of body wt is considered to be lethal amount of plant material. ... /Cyanogenic plants/ [Booth, N.H., L.E. McDonald (eds.). Veterinary Pharmacology and Therapeutics. 5th ed. Ames, Iowa: Iowa State University Press, 1982. 961].

Aliphatic nitriles have been postulated to manifest their

toxicity through cyanide (CN) liberation. The signs of toxicity and effect of equitoxic LD50 doses of saturated and unsaturated aliphatic mono- and dinitriles on tissue and blood CN levels, tissue glutathione levels and cytochrome c oxidase activities were studied in rats. Signs of toxicity were classified into cholinomimetic effects observed with unsaturated nitriles and CNS effects observed with saturated potassium cyanide. Hepatic and blood CN levels 1 hr after treatment were highest following malononitrile and decreased in the order οf propionitrile > potassium cyanide > acrylonitrile > butyronitrile allylcyanide fumaronitrile > acetonitrile. The order differed in brain where potassium cyanide preceded malononitrile and PCN. Hepatic and cytochrome c oxidase were significantly inhibited and corresponded to their CN levels. No significant inhibition of cytochrome c oxidase was observed in vitro. Acrylonitrile was the only nitrile which significantly reduced tissue GSH levels. Toxic expression of aliphatic nitriles depended on CN release and their degree of unsaturation. With unsaturated aliphatic nitriles CN release played a minimal role in their toxicity. /Cyanides/ [Ahmed AE, Farooqui M YH; Toxicol Lett (AMST) 12 (2-3): 157-64 (1982)].

Acute toxicity and metabolism of 7 dinitriles in mice was studied in relation to the chemical structures. The oral LD50 for each nitrile was detected under different conditions for mice pretreated with either carbon tetrachloride (CCl4) or olive oil. All test nitriles were metabolized into cyanide in vivo and in vitro. The cyanide level was variable among the compounds (0.35-0.74 ug cyanide/g brain) at death in the brains of mice, the from malononitrile and adiponitrile level comparable to that found in mice killed by dosing with potassium cyanide. After receiving each nitrile, the mean survival time of mice pretreated with CCl4 was prolonged and their brain cyanide level decreased when compared with the corresponding control. With malononitrile, the former did not significantly change and the latter decreased slightly. Brain cyanide levels of control mice at death showed a peak at the lower log P region, whereas CCl4 pretreated animals of remained independently of with the log P, exception malononitrile. Microsomal metabolism of nitriles to cyanide was greatly inhibited when microsomes were prepared from livers of mice pretreated with CCl4. The relationship between log (1/LD50-CC14), LD50 in mice pretreated with CCl4, and log P fits a parabolic plot. /Cyanides/ [Tanii H et al; Arch Toxicol 57 (2): 88-93 (1985)1.

Water Data Interpretation, Concentrations and Toxicity (All Water

Data Subsections Start with "W."):

## W.Low (Water Concentrations Considered Low):

Cyanide was not detectable in water and sediments of Yellowknife Bay, Canada, between 1974 and 1976, although the bay receives liquid effluents containing cyanides from an operating gold mine. Nondetection was attributed to rapid oxidation [517].

# W.High (Water Concentrations Considered High):

Wastewater from electroplaters had total cyanide, dissociable cyanide, complex cyanide, and thiocyanate concentrations of 0.2 (max 3.0), 0.07, 0.2, and 0.02 mg/L, respectively [517].

Wastewater from oil refineries had total cyanide, dissociable cyanide, complex cyanide, and thiocyanate concentrations of 0.01 (max 4.0), 0.0, 0.01, and 2.2 mg/L, respectively [517].

Wastewater from coking operations had total cyanide, dissociable cyanide, complex cyanide, and thiocyanate concentrations of 2.1, 0.3, 0.8, and 23.6 mg/L, respectively [517].

Wastewater/runoff from gold mills in Canada had total cyanide concentrations ranging from 0.3 to 26.5 mg/L [517]. Gold mine cyanide extraction leach ponds in California, Nevada, and Arizona had total cyanide concentrations usually of 200-300 mg/L, frequently of 700 mg/L, and occasionally of 9,000 mg/L [517].

## W.Typical (Water Concentrations Considered Typical):

Uncontaminated waters from rural watersheds and industrial areas were found to have concentrations of total cyanide of 0.003 mg/L and 0.02 mg/L, respectively [517].

Uncontaminated water from small watersheds covered with grasslands and forest and uninhabited by humans was found to have concentrations of total cyanide in the range of 0.0007-0.002 mg/L, with a maximum of 0.005 mg/L [517].

Uncontaminated water from U.S. water supplies (2,595 samples nationwide) had mean and maximum concentrations of total cyanide of 0.0009 mg/L and 0.008 mg/L, respectively [517].

Uncontaminated water from U.K. water supplies had mean and maximum concentrations of total cyanide of <0.05 mg/L

and 0.1 mg/L, respectively [517].

Treated effluent from wastewater treatment plants in Chicago had total cyanide, dissociable cyanide, complex cyanide, and thiocyanate concentrations of 0.005-0.03, 0.003-0.007, 0.002-0.02, and 0.006-0.03 mg/L, respectively [517].

Hydrogen cyanide (HCN) is a common industrial pollutant and frequently occurs in water at concentrations between 0.1 and several mg/L of free HCN [517].

Concentrations ranging between 30 and 60 ug total cyanides/L seem related to runoff, with cyanide peaks more frequent in fall and winter during periods of minimal runoff. In larger rivers, cyanide was low in winter owing to dilution by high runoff, but peaked in summer because of cyanide production by plants [517].

Based on EPA STORET data, the mean cyanide concentration in most surface waters tested in the U.S. is not greater than 3.5 ug/L; however, 37 of 50 states have locales where cyanide concentrations in ambient water are greater than 3.5 ug/L, exceeding 200 ug/L at locales in 7 of these states. Cyanide concentrations >1 ug/L were detected in the Great Lakes. Concentrations of cyanide at various points of the Ohio River and its tributaries range from <5 to 80 ug/L [755]. NOTE: [755] does not specify what form the cyanide was in.

Samples from the Ottawa River indicate concentrations of cyanide below 10 ug/L for both raw and treated water. Manitoba, 116 of 124 water sampling stations reported concentrations of cyanide in treated water to be less than 100 ug/L, with a median value of 30 ug/L. From 1965 to 1976 in British Columbia, the concentrations of total cyanide (90th percentile) for streams measurements), lakes (361 measurements) and marine waters (22 measurements) were 10, 40 and <10 ug/L, respectively. (The minimum detectable concentration for cyanide during this period was 10 ug/L) [754]. NOTE: [754] does not specify what form the cyanide was in.

Environmental concentration ranges for cyanide in Canadian surface waters are (in ug/L): Not Detected (detection limit = 0.5 ug/L) to 9.7 for the Pacific region, 1980-83 (based on 147 samples); <2 to 2.1 for the Western region, prior to 1980 (based on 33 samples); and <2 to 370 for the Central region, 1980-83 (based on 134 samples) [754]. NOTE: [754] does not specify what form the cyanide was in.

Data from the Nationwide Urban Runoff Program as of 1982 indicate that cyanide was found in 16% of the urban

runoff samples collected in 19 cities across the U.S. In samples where it was detected, the cyanide concentration ranged from 2 to 33 ug/L [755]. NOTE: [755] does not specify what form the cyanide was in.

**W.Con**cern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

**W.Gen**eral (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

EPA 1996 Integrated Risk Information System (IRIS) Database Information on free cyanide, CAS number 57-12-5 [893]:

Ambient Water Quality Criteria for Aquatic Organisms:

Acute Freshwater: 2.2E+1 ug/L [893].

Older Published Water Quality Criteria for Cyanide (CAS# 57-12-5): 22 ug/L [446,689].

Chronic Freshwater: 5.2E+0 ug/L [893].

Older Published Water Quality Criteria for CYANIDE (CAS# 57-12-5): 5.2 ug/L [446,689].

Acute Marine: 1E+0 ug/L [893].

Older Published Water Quality Criteria for CYANIDE (CAS# 57-12-5) [446]: 1.0 ug/L.

Discussion: The procedures described in the "Guidelines for Deriving Numerical National Water Ouality for the Criteria Protection Aquatic Organisms and Their Uses" indicate that, except possibly where a locally important species is very sensitive, saltwater organisms and their uses should not be affected unacceptably if the one concentration average cyanide does not exceed 1.0 ug/l more than once every three years on the average. /Cyanide/ (USEPA;

Ambient Water Quality Criteria Doc: Cyanide p.10 (1984) EPA 440-5-84-028) [366].

Chronic Marine: None Given [446,893].

Reference: 51 FR 8361 (03/11/86) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315 [893].

Discussion: Water quality criteria for the protection of aquatic life derived from a minimum data base of acute and chronic tests on a variety aquatic organisms. The data are assumed to be statistically representative and are used to calculate concentrations which will not have significant short- or long-term effects on 95% of the organisms exposed. Recent criteria (1985 later) contain duration and frequency stipulations: the acute criteria maximum concentration is a 1-hour average and the chronic criteria continuous concentration is a 4-day average which are not to be exceeded more than once every 3 years, on the average (see Stephen et al., 1985). Earlier criteria (1980-1984) contained instantaneous acute and 24-hour average chronic concentrations which were not to be exceeded [893].

procedures described The in the for Numerical "Guidelines Deriving National Water Quality Criteria for the Protection of Aquatic Organisms and Their indicate that, except possibly where a locally important species is very sensitive, freshwater aquatic organisms and their uses should not be affected unacceptably if the four day average concentration of cyanide does not exceed 5.2 ug/l more than once every three years on the average and if the one hour average concentration does not exceed 22 ug/l more than once every three years on the average. /Cyanide/ (USEPA; Ambient Water Quality Criteria Doc: Cyanide p.10 (1984) EPA 440/5-84-028) [366].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the

replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

For CAS 57-12-5, CYANIDE (uq/L):

NATIONAL AMBIENT WATER QUALITY CRITERION - ACUTE: 22

NATIONAL AMBIENT WATER QUALITY CRITERION - CHRONIC: 5.2

SECONDARY ACUTE VALUE: No information found.

SECONDARY CHRONIC VALUE: No information found.

LOWEST CHRONIC VALUE - FISH: 7.8

LOWEST CHRONIC VALUE - DAPHNIDS: No information found.

LOWEST CHRONIC VALUE - NON-DAPHNID INVERTEBRATES: 18.33

LOWEST CHRONIC VALUE - AQUATIC PLANTS: 30

LOWEST TEST EC20 - FISH: 5.3

LOWEST TEST EC20 - DAPHNIDS: No information found.

SENSITIVE SPECIES TEST EC20: 1.17

POPULATION EC20: 11

Proposed free cyanide criteria suggest that sensitive species of aquatic organisms are protected at <3 ug/L [517].

Proposed free cyanide criteria for the protection of marine organisms [517]:

Adverse effects from chronic exposure: >2 ug free cyanide/L seawater [517].

Minimal risk: <5 ug free cyanide/L seawater

[517].

Hazardous: >10 ug free cyanide/L seawater
[517].

Lethal: >30 ug free cyanide/L seawater [517].

# W.Plants (Water Concentrations vs. Plants):

Adverse effects for algae and macrophytes were reported at >160 ug free cyanide/L [517].

For more details on cyanide effects on algae and macrophytes, see Eisler [517].

# W.Invertebrates (Water Concentrations vs. Invertebrates):

Proposed free cyanide criteria for the protection of invertebrates [517]:

Reduced amphipod survival: >3-34 ug free cyanide/L [517].

Hazardous concentrations to microorganisms: >300 ug free cyanide/L [517].

Reduced survival in bivalve mollusc larvae from chronic exposure: >14 ug free cyanide/L [517].

Among invertebrates, adverse nonlethal effects were documented between 18 and 43 ug/L, and lethal effects between 30 and 100 ug/L--although some deaths were recorded in the range 3 to 7 ug/L for the amphipod Gammarus pulex [517].

The 96-hour LC50 for a copepod was 30 ug HCN/L [517].

Two 96-hour LC50s for daphnids were 160 and 83 ug HCN/L [517].

Daphnia: 50% immobilization after 48 hr at 1.8 mg HCN/l. /Conditions of bioassay not specified/ (Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742) [366].

The 96-hour LC50 for mysid shrimp ranged from 93 to 113 ug HCN/L [517].

The 96-hour LC50 for a snail was 432 ug HCN/L [517].

Oyster motor activity was suppressed after 10 min of exposure to 150 ug HCN/L [517].

The LC20 (after 14 days of exposure) for a mussel species was 100 ug HCN/L [517].

For more details on cyanide effects on invertebrates, see Eisler [517].

The following information from HSDB [366] is for hydrogen cyanide (HCN):

LC50 Goniobasis livescens (snail) 760,000 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

LC50 Lymnaea emarginata (snail) 3,300 ug/1/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

LC50 Lymnaea sp, (snail, embryo) 51,900 ug/l/96 hr [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

LC50 Physa integra (snail) 1,350 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

LC50 Stemonema rubrum (mayfly) 500 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

LC50 Hyfropsyche sp (caddisfly) 2,000 ug/1/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-20 (1980) EPA 440/5-80-037].

## W.Fish (Water Concentrations vs. Fish):

Proposed free cyanide criteria for the protection of fish [517]:

A safe concentration for most freshwater fish species: 3.5 ug free cyanide/L (24-hr ave, not to exceed 52 ug/l at any time) [517].

Minimal impairment for most freshwater fish

species: 3-5 ug free cyanide/L [517].

Significant impairment for most freshwater fish species occurs at 8-16 ug free cyanide/L (exposed for at least 20 days) [517].

Impaired reproduction in sensitive species of freshwater fish: >25 ug free cyanide/L [517].

Hazardous concentrations for most freshwater fish species are >11 ug free cyanide/L [517]. Reduced survival after chronic exposure occurs in many freshwater fish species at 30-150 ug free cyanide/L [517].

Impaired swimming ability, growth, development, and behavior in freshwater fish: >100 ug free cyanide/L [517].

Lethal to rapidly lethal acute exposure: 300-1000 ug free cyanide/L [517].

Fish were the most sensitive aquatic organisms tested under controlled conditions. Significant adverse nonlethal effects, including reduced swimming performance and inhibited reproduction, were observed in the range of 5.0 to 7.2 ug free cyanide/L; deaths were recorded for most species between 20 and 76 ug free cyanide/L [517].

Reproductive impairment in adult bluegills (Lepomis macrochirus) has been reported following exposure to 5.2 ug CN/L for 289 days. Fertilized fish eggs are usually resistant to cyanide prior to blastula formation, but delayed effects occur at 60 to 100 ug HCN/L, including birth defects and reduced survival of embryos and newly hatched larvae [517].

Concentrations as low as 10 ug HCN/L caused developmental abnormalities in embryos of Atlantic salmon after extended exposure [517].

Free cyanide concentrations between 50 and 200 ug/L were fatal to the more-sensitive fish species over time, and concentrations >200 ug/L were rapidly lethal to most species of fish. Cyanide-induced subcutaneous pathology in fish includes hemorrhaging, liver necrosis, and hepatic damage. Exposure of fish for 9 days to 10 ug HCN/L was sufficient to induce extensive necrosis in the liver, although gill tissue showed no damage. Intensification of liver histopathology was evident at dosages of 20 and 30 ug HCN/L and exposure periods up to 18 days. Cyanide has a strong,

immediate, and long-lasting inhibitory effect on the swimming ability of fish. Free cyanide concentrations as low as 10 ug/L can rapidly and irreversibly impair the swimming ability salmonids in well-aerated water. Osmoregulatory disturbances recorded at 10 ug HCN/L may affect migratory patterns, feeding, and predator avoidance. general, fish experience In significant reduction in relative performance (based on osmoregulation, growth, swimming, and spermatogenesis) at 10 ug HCN/L, and although fish can survive indefinitely at 30 ug HCN/L in the laboratory, different the physiological requirements necessary to survive in nature could not be met. Increased predation by green sunfish (Lepomis cyanellus) on fathead minnows (Pimephales promelas) was noted at sublethal concentrations of HCN, but it was uncertain if fatheads became easier prey or if green sunfish had greater appetites [517].

The 96-h toxicity of mixtures of sodium cyanide and nickel sulfate to fathead minnows is influenced by water alkalinity and pH. Toxicity decreased with increasing alkalinity and pH from 0.42 mg CN/L at 5 mg CaCO3/L and pH 6.5, to 1.4 mg CN/L at 70 mg CaCO3/L and pH 7.5, to 730 mg CN/L at 192 mg CaCO3/L and pH 8.0 [517].

The 96-hour LC50 ranges for bluegill juveniles, fry, eggs, and eggs at hatching were 56-227, 109-218, 232-365, and 535-690 ug HCN/L, respectively [517].

Sperm motility in rainbow trout was affected at 1.0 ug HCN/L [517]. For more details on cyanide effects on rainbow trout, see Eisler [517].

The 96-hour LC50 for largemouth bass was 101 ug HCN/L [517].

The 96-hour LC50 ranges for yellow perch juveniles and for eggs and fry were 76-108 and 288->389 ug HCN/L, respectively [517].

Cyanide effects on fathead minnows ranged from 18 to 352 ug HCN/L [517]. For more details on cyanide effects on fathead minnows, see Eisler [517].

Cyanide effects on Atlantic salmon ranged from 5 to 100 ug HCN/L [517]. For more details on cyanide effects on Atlantic salmon, see Eisler [517].

Cyanide effects on brook trout ranged from 5 to 518

ug HCN/L [517]. For more details on cyanide effects on brook trout, see Eisler [517].

For more details on cyanide effects on other species of fish, see Eisler [517].

The following information from HSDB [366] is for hydrogen cyanide (HCN):

TLm Pinperch 0.069 mg/l/24 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

TLm Lepomis humilis (sunfish) 0.18 mg/l/24 hr /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

TLm Pinperch 0.05 mg/l/24 hr (in seawater) /Conditions of bioassay not specified/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

LTC Lepomis macrochirus (bluegill eggs) 535-693 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

LC50 Lepomis macrochirus (bluegill swim up fry) 232-365 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

LC50 Lepomis macrochirus (bluegill, juvenile) 75-125 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

LC50 Perca flavescens (yellow perch eggs) >276-389 ug/1/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

LC50 Perca flavescens (yellow perch, juvenile) 76-108 ug/1/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental

- Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salvelinus fontinalis (brook trout eggs) >212 to >242 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salvelinus fontinalis (brook trout, sac fry) 108-518 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salvelinus fontinalis (brook trout, swim up fry) 56-106 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salvelinus fontinalis (brook trout, juvenile) 53-143 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salmo gairdnerii (rainbow trout) 57 ug/1/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Pimephales promelas (fathead minnow eggs) 121-352 ug/1/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Pimephales promelas (fathead minnow, swim up fry) 82-122 ug/l/hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Pimephales promelas (fathead minnow, juvenile) 82-137 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

- LC50 Pimephales promelas (fathead minnow, juvenile, wild stock) 157-191 ug/l/96 hr, flow-through bioassay [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].
- LC50 Salmo gairdneri (rainbow trout) 68 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-21 (1980) EPA 440/5-80-037].
- LC50 Pimephales promelas (fathead minnow) 240 ug/1/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-23 (1980) EPA 440/5-80-0371.
- LC50 Pimephales promelas (fathead minnow, juvenile) 120 ug/1/5 days /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-23 (1980) EPA 440/5-80-037].
- LC50 Pimephales promelas (fathead minnow, juvenile) 123 ug/l/96 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-24 (1980) EPA 440/5-80-037].
- LC50 Lepomis macrochirus (bluegill, juvenile) 134 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-25 (1980) EPA 440/5-80-037].
- LC50 Lepomis macrochirus (bluegill, juvenile) 154 ug/1/72 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-25 (1980) EPA 440/5-80-037].
- LC50 Lepomis macrochirus (bluegill) 160 ug/l/48 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-25 (1980) EPA 440/5-80-037].
- LC50 Perca flavescens (yellow perch, embryo) 281 ug/l/96 hr /Conditions of bioassay not specified/ [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.B-26 (1980) EPA 440/5-80-037].

**W.Wild**life (Water Concentrations vs. Wildlife or Domestic Animals):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (see Tis.Wildlife, B) for these). To be considered unlikely to represent an ecological risk, water concentrations should be below the following benchmarks for each species present at the site [650]:

CAS 57-12-5 CYANIDE (AS POTASSIUM CYANIDE)

	WATER CONCEN-
SPECIES	TRATION (ppm)
Rat (test species)	0.0000
Short-tailed Shrew	81.3500
Little Brown Bat	140.6050
White-footed Mouse	52.5740
Meadow Vole	92.0140
Cottontail Rabbit	43.5990
Mink	45.2120
Red Fox	32.2670
Whitetail Deer	18.0530

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

Proposed free cyanide safe-level criteria for the protection of waterfowl [517]: <50 mg/L

Adverse nonlethal effects in mammals were noted at drinking water concentrations >150 mg HCN/L [517].

Many species of migratory birds were found dead in the immediate vicinity of gold-mine heap-leach extraction facilities and tailings ponds, presumably as a result of drinking the cyanide-contaminated (>200 mg total cyanide/L) waters [517].

Livestock found dead near a cyanide disposal site

had been drinking surface water runoff from the area that contained up to 365 mg HCN/L [517].

W.Human (Drinking Water and Other Human Concern Levels):

EPA 1995 Region 9 Tap Water Preliminary Remediation Goal: 730 ug/L free cyanide [868]. Different values have been published for other cyanide compounds [868].

EPA 1996 Integrated Risk Information System (IRIS) Database Information on free cyanide, CAS number 57-12-5 [893]:

Maximum Contaminant Level Goal:

Value: 0.2 mg/L [893]. Value: 0.2 mg/L for amenable cyanide [952].

Status/Year: Proposed 1990 Econ/Tech?: No, does not consider economic or technical feasibility Reference: 55 FR 30370 (07/25/90) [893].

Contact: Health and Ecological Criteria Division / (202)260-7571 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: EPA is proposing to regulate cyanide based on its potential adverse effects reported in a 2-year study in rats. The MCLG is based upon a DWEL of 0.76 mg/L and an assumed drinking water contribution of 20 percent. [893].

Maximum Contaminant Level (MCL)

Value: 0.2 mg/L [893,952].

Status/Year: Proposed 1990 Econ/Tech?: Yes, does consider economic or technical feasibility Reference: 55 FR 30370 (07/25/90) [893].

Contact: Drinking Water Standards Division / OGWDW / (202)260-7575 Safe Drinking Water Hotline / (800)426-4791 [893].

Discussion: EPA is proposing an MCL equal to the proposed MCLG of 0.2 mg/L.

[893].

Ambient Water Quality Criteria for Human Health [893]:

Water & Fish: 2E+2 ug/liter [893].

Older Values: Water Quality Criteria for CYANIDE (CAS# 57-12-5):

Human Health (1E-06 Risk Level for Carcinogens):

Published Criteria for Water and Organisms: 200 ug/L [446,689].

IRIS Recalculated (9/90) Criteria for Water and Organisms: 700 ug/L [446].

Fish Only, 1996: None Given [893].

Older Values: Water Quality Criteria for CYANIDE (CAS# 57-12-5):

Human Health (1E-06 Risk Level
for Carcinogens):

IRIS Recalculated (9/90) Criteria for Organisms Only: 21,500 ug/L [446]. IRIS Recalculated (7/93) Criteria for Organisms Only: 220,000 [689].

Reference: 45 FR 79318 (11/28/80) [893].

Contact: Criteria and Standards Division / OWRS / (202)260-1315 [893].

Discussion: This value is the same as the drinking water standard and approximates a safe level assuming consumption of contaminated organisms and water [893].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest one. Work on the replacement for the Gold Book [302] was underway in March of 1996, and IRIS is updated monthly [893].

Maximum allowable drinking water limits [517]:

U.S.: 10 ug free cyanide/L
Canada: <20 ug free cyanide/L</pre>

Lifetime health advisory for drinking water [517]:

<154 ug free cyanide/L.

10-day health advisories [517]:

Child: <220 ug free cyanide/L Adult: <770 ug free cyanide/L

State Drinking Water Standards [755]:

AZ: 220 ug/L KS, MN, NH,VT: 154 ug/L MA: 140 ug/L RI: 150 ug/L

W.Misc. (Other Non-concentration Water Information):

No information found.

**Sed**iment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

Cyanide has been found in sediments draining into Soda Butte Creek from McLaren (gold mining) Tailings upstream of Yellowstone Park, at a concentration of 0.23 mg/Kg dry weight (Del Nimmo, National Biological Survey, personal communication, 1995).

Proposed criteria for total cyanide in Great Lakes sediment [347,517,761]:

Moderately polluted: 0.1-0.25 mg total cyanide/kg dry weight

Heavily polluted: >0.25 mg total cyanide/kg dry weight

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of cyanide was 748.5 ppm (dry weight) [347].

Sed. Typical (Sediment Concentrations Considered Typical):

Proposed criteria for total cyanide in Great Lakes sediment [517,761]:

Non-polluted: <0.10 mg total cyanide/kg dry weight

**Sed.Con**cern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

**Sed.Gen**eral (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Sediment Concentrations. To be considered unlikely to represent an ecological risk, field concentrations should be below the following benchmark [652]:

For CAS 57-12-5, CYANIDE ANION, the sediment benchmark is 0.1 mg/kg dry weight (EPA REGION V).

Ontario lowest effect level 0.1 ug/kg (ppb) dry weight [761].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act for free cyanide (1982): 1 ppm indicates background concentrations. 10 ppm indicates moderate soil contamination. 100 ppm indicates threshold values that require immediate cleanup [347].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act for complex cyanide (1982): 5 ppm indicates background concentrations. 50 ppm indicates moderate soil contamination. 500 ppm indicates threshold values that require immediate cleanup [347].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

**Sed.Inv**ertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

**Sed.Wild**life (Sediment Concentrations vs. Wildlife or Domestic Animals):

No information found.

Sed. Human (Sediment Concentrations vs. Human):

No information found.

Sed.Misc. (Other Non-concentration Sediment Information):

No information found.

**Soil** Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

Proposed criteria for free cyanide in soil [517]:

Moderate contamination: 10 mg/kg dry weight Requires cleanup: 100 mg/kg dry weight

Proposed criteria for complex cyanide in soil [517]:

Moderate contamination: 50 mg/kg dry weight Requires cleanup: 100 mg/kg dry weight

Analyses of sewage sludges from 50 publicly owned treatment works by the U.S. Environmental Protection Agency (1985): The mean concentration of cyanide was 748.5 ppm (dry weight) [347].

Soil.Typical (Soil Concentrations Considered Typical):

Proposed criteria for free cyanide in soil [517]:

Background: 1 mg/kg dry weight

Proposed criteria for complex cyanide in soil [517]:

Background: 5 mg/kg dry weight

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and

Other Soil Benchmarks:

**Soil.Gen**eral (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

No information found.

Soil.Plants (Soil Concentrations vs. Plants):

No information found.

**Soil.Inv**ertebrates (Soil Concentrations vs. Invertebrates):

Bacteria exposed to cyanide may exhibit decreased growth, altered cell morphology, decreased motility, mutagenicity, and altered respiration. Mixed microbial populations capable of metabolizing cyanide and not previously exposed to cyanide were adversely affected at 0.3 mg HCN/kg; however, these populations can become acclimatized to cyanide and can then degrade wastes with higher cyanide concentrations [517].

**Soil.Wild**life (Soil Concentrations vs. Wildlife or Domestic Animals):

No information found.

Soil.Human (Soil Concentrations vs. Human):

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 1600 mg/kg "amenable cynanide" for ingestion pathway [952].

SSL = none given for inhalation pathway [952].

SSL = 2 to 40 mg/kg "amenable cyanide" for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

EPA 1995 Region 9 Preliminary remediation goals (PRGs), for free cyanide 1995 [868]:

Residential Soil: 1.3E+03 free cyanide mg/kg wet wt.

Industrial Soil: 1.4E+04 free cyanide mg/kg wet wt.

#### NOTE:

Different values have been published for other cyanide compounds [868].

PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.

Values are based on a non-carcinogenic hazard quotient of one.

PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects [903].

EPA 1995 Region 3 Risk based concentration (RBC) to protect from transfers to groundwater [903]: None given.

Soil.Misc. (Other Non-concentration Soil Information):

No information found.

**Tis**sue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

#### Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

For details on cyanide concentrations in a variety of cyanogenic plants, see also Eisler [517].

Cassava, also known as manioc, tapioca, yuca, or guacamate, is one of the very few--and, by far, the most important--food crops in which the cyanide content creates toxic problems [517].

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

See also Uses/Sources. Also, for details on cyanide concentrations in a variety of cyanogenic plants, see Eisler [517].

The hydrocyanic acid content of peeled cassava tubers from various localities in Eastern Nigeria (major cassava growing and consuming area) varied from 26 + or - 1.6 to 8 + or - 2.6 mg/100 g fresh weight. There was no correlation between the cyanide contents of cassava tubers and locality. (Ezeala DO, Okoro N; J Food Biochem 10, 2: 125-32, 1986) [366].

## Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

No information found.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Cyanogenic arthropods include two species of millipedes and the Zygaenid moth. Total cyanide concentrations in these are 428, 18, and 668 mg/kg wet weight, respectively [517].

### Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

No information found.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Cyanide concentrations in fish from streams that were deliberately poisoned with cyanide ranged between 10 and 100 ug total cyanide/kg whole body FW. Total cyanide concentrations in gill tissues of salmonids under widely varying conditions of temperature, nominal water concentrations, and duration of exposure ranged from about 30 ug/kg FW

to >7,000 ug/kg. Unpoisoned fish usually contained <1 ug/kg FW in gills, although values up to 50 ug/kg occurred occasionally. Lowest cyanide concentrations in gill occurred at elevated (summer) water temperatures; at lower temperatures, survival was greater and residues were higher. Fish retrieved from cyanide-poisoned environments, dead or alive, can probably be consumed by man because muscle cyanide residues were considered to be low (i.e., <1,000 mg/kg FW) [517].

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

No information found.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Wildlife derived from No-Observed-Adverse-Effect (NOAEL) levels (mg contaminant per kg body weight per day). To be considered unlikely to represent an ecological risk, wet-weight field concentrations should be below the following (right column) benchmarks for each species present at the site [650]:

CAS 57-12-5 CYANIDE (AS POTASSIUM CYANIDE)

	NOAEL	FOOD CONCEN-
SPECIES	(mg/kg/day)	TRATION (ppm)
Rat (test species)	6.87000	0.0000
Short-tailed Shrew	17.89700	29.8280
Little Brown Bat	22.49700	67.4900
White-footed Mouse	15.77200	102.0550
Meadow Vole	12.54700	110.4160
Cottontail Rabbit	4.21500	21.3400
Mink	4.47600	32.6720
Red Fox	2.72500	27.2480
Whitetail Deer	1.18200	38.3890

Comment: Actually, the number of significant figures for a benchmark value should never be more than one; even if these values have been taken directly from another report, they should be

rounded; otherwise the impression is given of a level of accuracy that is simply unwarranted. The uncertainties are too large to justify such a fine distinction (Owen Hoffman, SENES Oak Ridge, Personal Communication, 1997).

Proposed free cyanide criteria suggest that sensitive species of birds and livestock are protected at <100 mg/kg diet [517].

Proposed total cyanide criteria for livestock diet (safe level) [517]: <625 mg/kg wet wt.

Adverse nonlethal effects in mammals were noted at dietary concentrations >720 mg HCN/kg ration [517].

Animals that eat rapidly are at greatest risk, and intakes of 4 mg HCN/kg BW can be lethal if consumed quickly [517].

Free cyanide levels associated with high avian death rates include 0.12 mg/L in air, 2.1-4.6 mg/kg body weight (BW) via acute oral exposure, and 1.3 mg/kg BW administered intravenously. Dietary levels of 135 mg total cyanide/kg ration resulted in growth reduction of chicks, but 103 mg total cyanide/kg ration had no measurable effect on domestic chickens [517].

For details on cyanide effects on several species of birds, and on livestock, wildlife, and test animals, see Eisler [517].

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

No information found.

### Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

Food Survey Results [366]:

The nutritive value of African star apple, C albidum, was evaluated chemically. ... The hydrocyanic acid content was 5.4 mg/100 g in the peel and 6.8 mg/100 g in the pulp. ... The contribution of the fruit of African star apple to the nutrient requirements of consumers and other possible uses for the

fruit are discussed. [Edem DO et al; Food Chem 14 (4): 303-12 (1984)].

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

EPA 1996 Integrated Risk Information System (IRIS) Database Information on free cyanide, CAS number 57-12-5 [893]:

Crit. Dose: 10.8 mg/kg-day [Study 1 NOAEL] UF: 100 MF: 5

RfD for free cyanide: 2E-2 mg/kg-day [893,868,952]. Different values have been published for other cyanide compounds [868].

Confidence: Medium [893].

For details on cyanide effects on humans, see Eisler [517].

Proposed free cyanide criteria suggest that human health is protected at concentrations of <50 mg/kg diet [517].

A fatal dose of cyanide to humans is only 60-90 mg [483].

Proposed free cyanide criteria in human food items (mg/kg) [517]:

Cocoa	<20 dry weight
Beans, nuts	<25 dry weight
Cereals, grains	<25 dry weight
Citrus fruits	<50 wet weight
Uncooked pork	<50 wet weight
Grains	<75 wet weight
Cereal flours	<125 dry weight
Spices	<250 wet weight
Frozen meat	<950 wet weight
Bakery products, yeast	<1,500 dry weight
Egg white solids	<1,000 dry weight

## Allowable Tolerances [366]:

Tolerances for residues of the insecticide hydrogen cyanide from post harvest fumigation are established as follows: 250 ppm in or on the following spices: Allspice, anise, basil, bay, black pepper, caraway, cassia, celery seed, chili, cinnamon, cloves, coriander, cumin, dill, ginger, mace, marjoram, nutmeg,

oregano, paprika, poppy, red pepper, rosemary, sage, savory, thyme, tumeric, white pepper; 75 ppm in or on barley, buckwheat, corn (including popcorn); milo (grain sorghum), oats, rice, rye, wheat; 50 ppm in or on citrus fruits; 25 ppm in or on almonds, beans (dried), cashews, cocoa beans, peanuts, peas (dried), pecans, sesame, walnuts. [40 CFR 180.130 (7/1/88)].

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

Normal concentrations of total cyanide in human blood are <0.2 mg/kg wet wt. [517].

## Tis.Misc. (Other Tissue Information):

Higher plants are adversely affected by cyanide through cytochrome oxidase inhibition; the rate of production and release of cyanide by plants to the environment through death and decomposition is unknown [517].

Birds that feed predominantly on flesh were more sensitive to cyanide than were herbivores [517].

Deer (Odocoileus sp.) and elk (Cervus sp.) have been observed to graze on forages that contain a high content of cyanogenic glycosides; however, cyanide poisoning has not been reported in these species [517].

**Bio.Detail:** Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

Most authorities now agree that: (1) cyanide has low persistence in the environment and is not accumulated or stored in any mammal studied; (2) cyanide biomagnification in food webs has not been reported, possibly due to rapid detoxification of sublethal doses by most species, and death at higher doses [517].

Cyanides are readily absorbed through inhalation, ingestion, or skin contact and are readily distributed throughout the body via blood [517].

## Biological Half-Life [366]:

Half-life for the conversion of cyanide to thiocyanate from a non-lethal dose in man is between 20 min and 1 hr. /Cyanide/ [Feldstein M, Klendshoj NC; J Lab Chin Med 44: 166-70 (1954) as cited in NIOSH; Criteria Document: Hydrogen Cyanide and Cyanide Salts p.45 (1976) DHEW Pub. NIOSH 77-108].

### **Int**eractions:

Additive or more-than-additive toxicity of free cyanide to aquatic fauna has been reported in combination with ammonia or arsenic. However, conflicting reports on the toxicity of mixtures of HCN with zinc or chromium require clarification. Formation of the nickelocyanide complex markedly reduces the toxicity of both cyanide and nickel at high concentrations in alkaline pH. At lower concentrations and acidic pH, solutions increase in toxicity by more than 1,000X, owing to dissociation of the metallocyanide complex to form hydrogen cyanide. Mixtures of cyanide and ammonia may interfere with seaward migration of Atlantic salmon smolts under conditions of low dissolved oxygen [517].

There is general agreement that cyanide is more toxic to freshwater fish under conditions of low dissolved oxygen; that pH levels within the range 6.8 to 8.3 had little effect on cyanide toxicity but enhanced toxicity at acidic pH; that juveniles and adults were the most sensitive life stages tested and embryos and sac fry the most resistant; and that substantial interspecies variability exists in sensitivity to free cyanide. Initial dose and water temperature both modify the biocidal properties of HCN to freshwater teleosts. At slowly lethal concentrations (i.e., <10 ug HCN/L), cyanide was more toxic at lower temperatures; at high, rapidly lethal HCN concentrations, cyanide was more toxic at elevated temperatures. By contrast, aquatic invertebrates were most sensitive to HCN at elevated water temperatures, regardless of dose. Season and exercise modify the lethality of HCN to juvenile rainbow trout; higher resistance to cyanide correlated with higher activity induced by exercise and higher temperatures, suggesting a faster detoxification rate or higher oxidative and anaerobic metabolisms [517].

An increase in temperature increases the toxicity of cyanide, and an increase of 10 degrees C will produce a two- to threefold increase in the rate of lethal action of cyanide [302].

### Uses/Sources:

About 84% of domestic HCN production is used to produce organic cyanides, also known as nitriles, including acrylonitriles, methyl methacrylate, and adiponitrile [517].

In addition to their primary use in the metals and electroplating industries, and in the manufacture of synthetic fibers and plastics, various cyanide compounds have been used directly or as an intermediate to produce synthetic rubber, fumigants, rodenticides, insecticides, predator control agents, rocket fuels, paints and paint finishes, paper, nylon, pharmaceuticals, photographic chemicals, mirrors, cement, perfume, bleaches, soaps and detergents, riot control agents, fertilizers, and weedicides [517].

Hydrogen cyanide vapor, because of its high and rapid acute lethal toxicity and ready diffusion, has been used widely to fumigate buildings, ships, and warehouses; to exterminate rabbits, rodents, and large predators; and in horticultural practice, to control insect pests that have developed resistance to other pesticides [517].

Sodium cyanide has been used for about 50 years by the U.S. Fish and Wildlife Service against coyote in attempts to protect livestock, especially sheep [517].

Cyanide compounds have been used to collect various species of In England and Scotland, cyanides are used freshwater fish. legally to control rabbits, and illegally to obtain Atlantic salmon (Salmo salar) and brown trout (Salmo trutta) from rivers, leaving no visible evidence of damage to the fish. Sodium cyanide has been applied to streams in Wyoming and Utah to collect fish through whitefish anesthesia; mountain (Prosopium williamsoni) sensitive to cyanide and died at concentrations that were tolerable to salmon and trout. Sodium cyanide was also used as a fish control agent in Illinois, Nebraska, South Dakota, Missouri, and in the lower Mississippi River valley, but was never registered for this use because of human safety concerns [517].

Road salt in some areas may contribute to elevated cyanide levels in adjacent surface waters. In climates with significant snowfall, road salt is applied as a deicing agent. Road salts are commonly treated with anticaking agents to ensure uniform spreading. One anticaking agent, sodium hexacyanoferrate, decomposes in sunlight to yield the highly toxic free cyanide that contaminates surface waters by runoff. Another anticaking agent, yellow prussiate of soda (sodium ferrocyanide), has been implicated in fish kills when inadvertently used by fish culturists [517].

Many species of plants, including some fungi, bacteria, algae, and higher plants, produce cyanide as a metabolic product [517].

In some cases, soil bacteria and fungi produce cyanides as secondary metabolites, with adverse effects on certain plants. Several species of arthropods normally contain elevated whole-body cyanide concentrations, and these confer protection against predators and allow consumption of cyanogenic plants [517].

Anthropogenic sources of cyanide in the environment include industrial processes, laboratories, fumigation operations, cyanogenic drugs, fires, cigarette smoking, and chemical warfare operations. Cyanides are present in many industrial wastewaters, especially those of electroplaters, manufacturers of paint, aluminum, and plastics, metal finishers, metallurgists, coal gasification processes, certain mine operations, and petroleum refiners [517].

Cyanide compounds are useful to society in terms of their key role in synthetic and industrial processes, for certain fumigation and agricultural uses, and for some therapeutic applications. Cyanide serves no useful purpose in the human body, yet it is present in our food, air, and water [517].

Natural sources of cyanide include various species of bacteria, algae, fungi, and higher plants that form and excrete cyanide. The most widely distributed major food crop with a high content of cyanogenic glycosides is cassava (Manihot esculenta), also known as manioc. Cassava is a staple food in human diets in over 80 countries, and it is sometimes added to animal feeds as a substitute for more expensive cereal grains. In humans, chronic cyanide intoxication caused by consumption of cassava is the main etiological factor in the debilitating tropical ataxic neuropathy. Other plants having comparatively elevated cyanide content include

fruit pits, sweet potatoes (Ipomoea batatas), corn (Zea mays), bamboo shoots (Bambos spp.), linseed, (Linum sp.), lima beans (Phaseolus lunatus), and millet (Panicum millaceum). In higher plants that contain cyanogenic glycosides, at least 20 of these compounds have been identified. Amygdalin--one of the more intensively studied cyanogenic glycosides -- is found in seeds of the cherry (Prunus spp.), plum (Prunus spp.), peach (Prunus persica), apricot (Prunus armeniaca), apple (Malus malus), pear (Pyrus laurel communis), and many parts of the cherry laurocerasus). Apricot seeds and peach kernels are food delicacies in Turkey, and have caused at least nine poisonings (two fatal) in children from that country. Acute cyanide poisoning has occurred in the United States from the ingestion of almond-flavored milkshakes prepared from apricot kernels. Amygdalin is also the chief ingredient in laetrile, a medication prescribed by some Both laetrile and amygdalinphysicians to control tumors. containing fruit pits have been implicated as the causes of acute cyanide poisoning in humans. Another naturally occurring group of organic cyanides (nitriles) is the highly toxic pseudocyanogenic glycosides, especially cycasin, and these have been implicated in a variety of tropical diseases of the nervous system, and partial or total blindness. Other nitriles found in plants include the lathyrogenic compounds, glucosinolates, and the cyanopyridine alkaloids [517].

For additional more detailed information, see Eisler [517].

# Forms/Preparations/Formulations:

See also Uses/Sources section above.

The chemical speciation of cyanides varies according to their source. Specific terms used to describe cyanide include free cyanide, cyanide ion, simple cyanides, complex cyanides, nitriles, cyanogens, and total cyanide. The most common forms of cyanide in the environment are free cyanide, metallocyanide complexes, and synthetic nitriles [517]. For details on these compounds, see Eisler [517] info in Chem.Detail section below.

Cyanide compounds may be grouped according to their physical and chemical properties as free, simple, complex and organic Cyanide ion refers to the single, free anion (CN-), excluding all other cyanide species. Molecular HCN (hydrogen cyanide, hydrocyanic acid) refers to cyanide in the form of an uncharged, undissociated molecule. Free cyanide refers to the summation of molecular HCN and the cyanide ion in aqueous solution, irrespective of their sources in water. (NOTE: Under typical temperature and pH environmental conditions, most (>90%) of the free cyanide would be present as HCN.) Simple cyanides are those compounds that dissociate directly in water to yield a cation and the cyanide ion, with no soluble intermediates. Complex cyanide may dissociate in water to a cation and an anion composed of two or more different chemical forms, one of which is cyanide. The anion is termed a complex ion and may be subject to further dissociation, possibly releasing free cyanide ions. Organic compounds containing the CN group are termed nitriles or cyanides, depending upon the nomenclature used [754].

The term "total cyanide" has been used in the literature to convey different ideas. From an operational viewpoint, total cyanide comprises all cyanide and some cyanate species (compounds containing the OCN group) or groups determinable by a particular, selected analytical method. Total cyanide also refers to the summation of the CN group in all the different forms of cyanide that exist in aqueous solution. Terms such as "total cyanide", "oxidizable cyanide", "cyanide amenable to chlorination" and "cyanide amenable to ozonation" reflect the corresponding methods of analysis [754].

Simple cyanides, such as alkali cyanides, readily dissociate in water to yield the cyanide ion, which then enters into equilibrium with HCN. It has been observed that there are 28 elements that may form complex cyanide compounds, and there are more than 68 oxidation states of these elements capable of forming complex cyanides. Hence, there exists the possibility of a multitude of complex metallocyanides that may occur in aqueous systems, each possessing unique physical and chemical properties [754].

Extremely toxic cyanides include the following compounds [354]:

Acrylonitrile (vinyl cyanide) Adiponitrile Benzyl cyanide Cyanogen bromide Cyanogen iodide Formaldehyde cyanohydrin Hydrocyanic acid (hydrogen cyanide) Isobutyronitrile Lactonitrile Malononitrile Methacrylonitrile Potassium cyanide Potassium silver cyanide Propionitrile Propionitrile, 3-chloro-Sodium cyanide

Note: various cyanide compounds have different CAS numbers and general hazard characteristics [868].

Chem. Detail: Detailed Information on Chemical/Physical Properties:

See also [754] information Forms/Preparations/Formulations section above for more on cyanides.

Hydrogen cyanide is a colorless, flammable liquid or gas that boils at 25.7 degrees C and freezes at minus 13.2 degrees C. The gas rarely occurs in nature, is lighter than air, and diffuses

rapidly; it is usually prepared commercially from ammonia and methane at elevated temperatures with a platinum catalyst. It is miscible with water and alcohol, but is only slightly soluble in ether. In water, HCN is a weak acid with the ratio of HCN to CN-about 100 at pH 7.2, 10 at pH 8.2, and 1 at pH 9.2. HCN can dissociate into H+ and CN-. Cyanide ion, or free cyanide ion, refers to the anion CN- derived from hydrocyanic acid in solution, in equilibrium with simple or complexed cyanide molecules. Cyanide ions resemble halide ions in several ways and are sometimes referred to as "pseudohaline" ions. For example, silver cyanide is almost insoluble in water, as are silver halides. Cyanide ions also form stable complexes with many metals [517].

Simple cyanides typically refer to alkali water-soluble salts, such as sodium cyanide, potassium cyanide, calcium cyanide, and mercury cyanide but also include several cyanide salts of alkali, alkaline earth, or heavy metals, that is, zinc cyanide, cadmium cyanide, nickel cyanide, and silver cyanide of varying degrees of solubility. In water, NaCN and KCN will completely dissociate to give free cyanide. All simple cyanides ionize in water to release cyanide ion which, depending on pH, will form hydrocyanic acid. For sodium cyanide, the reaction proceeds as follows:

- (1) NaCN --> Na+ + CN-
- (2) CN- + HOH --> HCN + OH-

Increased pH will maintain a larger fraction of the cyanide as CN-, and acidification will cause the reverse. At pH 7, about 99% of the free cyanide is in the form of HCN, whereas at pH 9.3 HCN composes 50%. Since HCN is extremely water soluble and is also one of the most toxic cyanide species, it is noteworthy that the toxicity of simple cyanides will not be affected measurably below pH 8.3 [517].

Complex cyanides are compounds in which the cyanide anion is incorporated into a complex or complexes; these compounds are different in chemical and toxicologic properties from simple cyanides. In solution, the stability of the cyanide complex varies with the type of cation and the complex that it forms. Some of these are dissociable in weak acids to give free cyanide and a cation, while other complexes require much stronger acidic conditions for dissociation. (For a listing of least-stable, moderately stable, and most stable complexes, see Eisler [517].) The toxicity of complex cyanides is usually related to their ability to release cyanide ions in solution, which then enter into an equilibrium with HCN; relatively small fluctuations in pH significantly affect their biocidal properties [517].

Cyanogen is the simplest compound containing the cyanide group. Cyanogen is an extremely toxic, flammable gas that reacts slowly with water to form HCN, cyanic acid, and other compounds; it is rapidly degraded in the environment. Cyanogen and its halide derivations are comparable in toxicity to hydrogen cyanide [517].

Nitriles are defined as organic compounds (RCN) containing the cyanide group. Cyanide bound to carbon as nitriles (other than as cyanogenic glycosides) are comparatively innocuous in the

environment, and are low in chemical reactivity and are biodegradable. For simple mononitriles there is a clear progression, with more cyanide being released as chain length A similar pattern exists in dinitriles, corresponding compounds require a longer carbon chain than mononitriles before free cyanide is produced. Based on studies with chicken liver homogenates, mononitriles were more toxic than dinitriles, and within each group the order of toxicity was CH3 > C2H5 > C3H7 > C4H9 > C5H11 > C7H15. Cyanohydrins [R2C(OH)CN] and cyanogenic glycosides [R1R2C(OR3)CN] are special classes nitriles, in that under appropriate conditions they will decompose to HCN and cyanide ions. Cyanogens (not to be confused with such acrylonitrile, priopionitrile, cyanogen), as succinonitrile, are nitrile-containing materials of complexity and lability, and can liberate free and toxicologically available amounts of cyanide. But the nonnitrile portion of the cyanogen molecule may exert an independent or interactive toxicity, causing a complex response [517].

Cyanates contain the OCN group. Inorganic cyanates that are formed industrially by the oxidation of cyanide salts hydrolyze in water to form ammonia and bicarbonate ion. Alkyl cyanates are insoluble (sic, actually "relatively insoluble") in water and form cyanurates. Alkyl isocyanates contain the OCN radical, are formed from cyanates, and, like cyanates, are readily hydrolyzed. Thiocyanates (SCN group) are formed from cyanides and sulfurcontaining materials and are relatively stable [517].

Total cyanides refers to all cyanide-containing compounds, including simple and complex cyanides, cyanoglycosides, and free cyanide. Total cyanides is a chemical measurement of free cyanide present in solution or released by acidification or digestion. Only free cyanide is considered to be a biologically meaningful expression of cyanide toxicity. Under most circumstances, the concentration of total cyanide will exceed that of HCN. In some waters, however, the total cyanide concentration may consist almost entirely of free cyanide, or it may contain cyanides that readily photodecompose or dissociate to yield HCN. The relation between total cyanide and free cyanide in natural waters varies with receiving-water conditions, type of cyanide compounds present, degree of exposure to daylight, and presence of other chemical compounds [517].

Hydrogen cyanide has frequently been associated with the odor of bitter almonds. The threshold odor for olfactory detection of atmospheric HCN is 1 mg/L, but the odor may not be detected for various reasons, including the presence of other odors, and the fact that only 20% to 40% of those tested could detect a cyanide odor [517].

The physical states of potassium cyanide (KCN), hydrogen cyanide (HCN), and sodium cyanide (NaCN) are solid, gas or liquid, and solid, respectively [517].

The solubilities in water of KCN, HCN, and NaCN are 716 g/L at 20 degrees C, miscible, and 480 g/L at 10 degrees C, respectively [517].

The boiling points of HCN and NaCN are 25.7 and 1496 degrees C, respectively [517].

The melting points of KCN, HCN, and NaCN are 634.5, -13.21, and 563.7 degrees C, respectively [517].

The specific gravities of KCN, HCN, and NaCN are 1.5, 0.7 (liquid), and 1.6, respectively [517].

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

#### WATER:

Little information is available on the fate of complex cyanides in natural waters. The role of precipitation and sorption in the removal of complex cyanides from the water column has not been adequately examined. Numerous metallocyanide complex ions are stable in aqueous solution in the absence of ultraviolet and visible light; in the presence of sunlight, however, photodecomposition of some complexes, with the resultant release of cyanide ions, may occur [754].

Much of the information regarding the fate of cyanides in the aquatic environment has been derived from studies where complex waste mixtures with high concentrations of cyanides were involved. It is, however, difficult and often misleading to extrapolate such information to natural conditions. From the limited information available under natural conditions, it cannot be assumed that cyanides have a short residence time in the aquatic environment [754].

Some complex metallocyanides may dissociate in water, generating complex cyanide ions which may further dissociate, releasing free cyanide ion. In general, many complex ions are more stable than their parent compounds, and, hence, subsequent dissociation to cyanide ions may be relatively minor. Iron-cyanide complex ions, for example, may dissociate to cyanide ions in the presence of sunlight below about pH 8 [754].

## SEDIMENTS:

Additional data are necessary to assess the significance of cyanide sorption to suspended solids and sediments in water. The existing data indicate that the adsorption of hydrogen cyanide to suspended solids and sediment will not be significant. However, soluble metal cyanides may show stronger adsorption than hydrogen cyanide. The extent of adsorption increases with decreasing pH and increases with increasing iron oxide, clay, and organic material contents of water. Adsorption is probably insignificant even for metal cyanides when compared to volatilization and biodegradation [755].

### SOILS:

Cyanide is not strongly adsorbed and retained in soils and leaching into surrounding groundwater will probably occur. Numerous microorganisms have been identified which are capable of degrading free cyanide [517,754].

Volatilization of hydrogen cyanide would be a significant loss mechanism for cyanides from soil surfaces at a pH <9.2 [755].

#### **GROUNDWATER:**

In cases where cyanide levels are toxic to microorganisms (i.e., landfills, spills), water-soluble cyanides may leach into groundwater [755].

Alkaline chlorination of wastewaters is one of the most widely used methods of treating cyanide wastes. In this process, cyanogen chloride, CNCl, is formed, which at alkaline pH is hydrolyzed to the cyanate ion, CNO-. If free chlorine is present, CNO- can be further oxidized. Other methods used in cyanide waste management include lagooning for natural degradation, evaporation, exposure to ultraviolet radiation, aldehyde treatment, ozonization, acidification-volatilization-reneutralization, ion exchange, activated carbon absorption, electrolytic decomposition, catalytic and biological treatment with cyanide-metabolizing oxidation. In the case of Canadian gold-mining operations, the bacteria. primary treatment for cyanide removal is to retain gold mill wastewaters in impoundments for several days to months; removal photodegradation, chemical occurs through volatilization, oxidation, and, to a lesser extent, microbial oxidation. Microbial oxidation of cyanide is not significant in mine tailing ponds, which typically have pH >10, a low number of microorganisms, low nutrient levels, large quiescent zones, and cyanide concentrations >10 mg/L [517].

Under aerobic conditions, cyanide salts in the soil are microbially degraded to nitrites or form complexes with trace metals. Under anaerobic conditions, cyanides denitrify to gaseous nitrogen compounds that enter the atmosphere [517].

Volatile cyanides occur only occasionally in the atmosphere, due largely to emissions from plating plants, fumigation, and other special operations. Under normal conditions cyanide has relatively low persistence in air, usually between 30 days and one year, although some atmospheric HCN may persist for up to 11 years. Data are lacking on the distribution and transformation of cyanide in the atmosphere and should be acquired [517].

Data on the recovery of poisoned ecosystems are scarce. In one case, a large amount of cyanide-containing slag entered a stream from the reservoir of a Japanese gold mine as a result of an earthquake. The slag covered the stream bed for about 10 km from the point of rupture, killing all stream biota; cyanide was detected in the water column for only 3 days after the spill. Within 1 month flora was established on the silt covering the above-water stones, but there was little underwater growth. After 6-7 months, populations of fish, algae, and invertebrates had recovered, although species composition of algae was altered [517].

Additional data are necessary to assess the significance of cyanide sorption to suspended solids and sediments in water. The existing data indicate that the adsorption of hydrogen cyanide to suspended solids and sediment will not be significant. However, soluble metal cyanides may show stronger adsorption than hydrogen cyanide. The extent of adsorption increases with decreasing pH and increases with increasing iron oxide, clay, and organic material contents of water. Adsorption is probably insignificant even for metal cyanides when compared to volatilization and biodegradation [755].

The following HSDB information is for hydrogen cyanide (HCN) only [366]:

# Terrestrial Fate [366]:

By analogy to the fate of cyanides in water, it is predicted that the fate in soil would be pH dependent. Cyanide may occur in the form of hydrogen cyanide, alkali metal salts, or immobile metallocyanide complexes. At soil surfaces with pH <9.2, it is expected that volatilization of hydrogen cyanide would be an important loss mechanism for cyanides. In subsurface soil, cyanide present at low concentrations would probably biodegrade. In soil with pH <9.2, hydrogen cyanide is expected to be highly mobile, and in cases where cyanide levels are toxic to microorganisms (ie, landfills, spills), this compound may leach into groundwater. [DHHS/ATSDR; Toxicological Profile for Cyanide (Draft) p.77 (1/88)].

# Atmospheric Fate [366]:

Most cyanide in the atmosphere is expected to exist almost entirely as hydrogen cyanide gas, although small amounts of metal cyanides may be present as particulate matter in air. The reaction of hydrogen cyanide with photochemically generated hydroxyl radicals proceeds fairly slowly. Based on a reaction rate constant of 3x10-14 cu m/(molecules-sec) at 25 deg C, and assuming an ambient hydroxyl radical concentration of molecules/cu m, the half-life for the reaction of hydrogen cyanide vapor with hydroxyl radicals in the atmosphere has been approximately 334 days. Hydrogen cyanide is expected to be resistant to direct photolysis. The relatively slow rate of degradation of hydrogen cyanide suggests that this compound has the potential to be transported over long distances before being removed by physical or chemical processes. Since hydrogen cyanide is miscible in water, it appears that wet deposition may be an important fate process. Metal cyanide particles are expected to be removed from air by both wet and dry deposition. [DHHS/ATSDR; Toxicological Profile for Cyanide (Draft) p.76 (1/88)].

## Volatilization from Water/Soil [366]:

Volatilization is expected to be an important (if not dominant) fate process for hydrogen cyanide. At pH <9.2, most of the free cyanide should exist as hydrogen cyanide, a volatile form of cyanide. Wide variations in the rate of volatilization are expected since this process is affected by a number of parameters including temperature, pH, wind speed, and cyanide concentration. Because of the lack of data on this topic, the half-life for this process could not be determined. [ATSDR; Toxicological Profile for Cyanide (Draft) p.77 (1/88)].

# Soil Adsorption/Mobility [366]:

Hydrogen cyanide is not strongly partitioned into the sediments or suspended adsorbents, primarily due to its high solubility in water. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 12-6].

Cyanide mobility is least where soils exhibit low pH, high concn of free iron oxides, and positively charged particles (eg, kaolin, chlorite, gibbsite). Mobility is greatest at high pH, high concn of free calcium carbonate (high negative charge) and low clay content. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 12-6].

Adsorption of hydrogen cyanide by montmorillonitic clays is fairly weak and is decreased by the presence of water. [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 12-61.

### Biodegradation [366]:

Waste water treatment; sludge digestion: at 25 mg/l: no adverse effect in 24 days; at 30 mg/l: initial retarding effect for 6 days; at 50 mg/l: 10% reduction in gas production. [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 742].

Bacteria and protozoa may degrade cyanide by converting it to carbon dioxide and ammonia. [Leduc G et al; Natur Can 100: 1 (1973) as cited in USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-24 (1980) EPA 440/5-

80-037].

Removal of free and complex cyanides and thiocyanates by Pseudomonas paucimobilis from wastewater was studied. [Mudder TI, Whitlock JL; US Patent No 4440644 (04/03/84) /assigned to:/ (Homestake Mining Co)].

# Abiotic Degradation [366]:

Cyanide is converted to cyanate during chlorination of water supplies. An alkaline pH favors the oxidation by chlorine, whereas an acid pH favors volatilization of hydrogen cyanide into the atmosphere. [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-25 (1980) EPA 440/5-80-0371.

the of titanium dioxide powder, In presence photocatalytic oxidation of cyanide proceeds significant rates in both high intensity artificial sunlight and unfocused sunlight. With titanium dioxide powder present, more than 99% of a 1 mM (26 mg/l) solution of cyanide ion was oxidized by exposure to sunlight for two days. In the absence of titanium dioxide powder, little or no oxidation occurred. [Callahan, M.A., Slimak, N.W. M.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 12-2].

Absorption, Distribution and Excretion for hydrogen cyanide (HCN) only [366]:

In 30 days, 72% of (14)c from ip dose of (14)c-cyanide to mice was excreted in urine & feces, 25% in expired air, & 3% was retained ... Peak excretion occurred within 10 min in expired air & within 6-24 hr in urine & feces. [The Chemical Society. Foreign Compound Metabolism in Mammals. Volume 1: A Review of the Literature Published Between 1960 and 1969. London: The Chemical Society, 1970. 94].

The cyanide ion is readily absorbed after oral or parenteral admin. Prolonged local contact with ... HCN may result in absorption of toxic amt through skin. Part of absorbed cyanide is excreted unchanged by the lung. Larger portion ... Converted by ... Sulfurtransferase to relatively nontoxic thiocyanate ion. /Cyanide/ (Goodman, L.S., and A. Gilman. [eds.) The Pharmacological Basis of Therapeutics. 5th ed. New York: Macmillan Publishing Co., Inc., 1975. 904].

Hydrogen cyanide vapor is absorbed rapidly through the lung. Because HCN has a pKa of 9.2 and exists primarily as the acid under biological conditions, absorption

across the alveolar membrane should be rapid. Human inhalation of 270 ppm HCN vapor brings death immediately, while 135 ppm is fatal after 30 minutes. [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-7 (1980) EPA 440/5-80-037].

Hydrogen cyanide, in either liquid or vapor form, is absorbed through the skin. Absorption is probably increased if the skin is cut, abraded, or moist. [USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-8 (1980) EPA 440/5-80-037].

Cyanide is distributed to all organs and tissues via the blood, where its concn in red cells is greater than that in plasma by a factor of two or three. Presumably, the accumulation of cyanide in erythrocytes is a reflection of its binding to methemoglobin. /Cyanides/ (USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-9 (1980) EPA 440/5-80-037].

A significant difference between the amount of cyanide in the whole blood of smokers and non-smokers could not be detected, but, the plasma thiocyanate levels of the smokers were significantly elevated. A ratio of cyanide to thiocyanate in body fluids was about 1 to 1000. A more reliable index of cyanide exposure may be measurement of plasma thiocyanate rather than determination of whole blood cyanide. [Pettigrew AR, Fell GS; Clin Chem 19: 466-71 (1973) as cited in NIOSH; Criteria Document: Hydrogen Cyanide and Cyanide Salts p.48 (1976) DHEW Pub. NIOSH 77-108].

The acute systemic toxicity of hydrogen cyanide, sodium cyanide and potassium cyanide by instillation into the inferior conjunctival sac was investigated. In the rabbit, the LD50 values in mmol/kg were 0.039 for HCN, 0.103 for sodium cyanide, and 0.121 for potassium cyanide. The acute lethal toxicity of sodium cyanide was not significantly different when applied as a solution or solid, and mixing the solid with an inert powder (kaolin) did not modify the toxicity. For all preparations, signs of toxicity appeared rapidly and death occurred within 3 to 12 min of the eye being contaminated. Cyanide concns in blood, serum, and various tissues were measured, and the results found compatible with a diagnosis of death from acute cyanide poisoning. Thus, following their instillation into the conjunctival sac, cyanides may be absorbed across conjunctival blood vessels in amounts sufficient to produce systemic toxicity. Contamination of the eye with cyanide could be a hazardous route of exposure. [Ballantyne B; J Toxicol, Cutaneous Ocul Toxicol 2 (2-3): 119-29 (1983)].

Hydrogen cyanide (HCN) was significantly more toxic than

sodium cyanide or potassium cyanide by im and transocular routes, and potassium cyanide significantly less toxic than HCN or sodium cyanide by skin penetration. Acute inhalation studies indicated a proportionately longer time to cause death at the lower concn, and thus larger total doses of HCN are required to cause death by lowconcn than by high-concn exposure. Following death by acute cyanide poisoning, whole blood concn are high and diagnostic significance; serum levels are 1/3-1/2 those in whole blood. Blood cyanide concn vary with the route, being lowest by inhalation and skin penetration. For a given exposure route, blood concn are similar for different species. Cyanide concn in certain specific tissues vary markedly with exposure route. [Ballantyne B; Dev Toxicol Environ Sci 11 (Dev Sci Pract Toxicol): 583-86 (1983)].

CN- forms complexes with a number of other chemicals (eg in tissues) & has strong affinity for cobalt. /Cyanide ion/ (Booth, N.H., L.E. McDonald (eds.). Veterinary Pharmacology and Therapeutics. 5th ed. Ames, Iowa: Iowa State University Press, 1982. 961].

Cyanides are rapidly absorbed from skin & all mucosal surfaces & are most dangerous when inhaled, because toxic amt are absorbed through bronchial mucosa & alveoli. /Cyanides/ (Haddad, L.M. and Winchester, J.F. Clinical Management of Poisoning and Drug Overdosage. Philadelphia, PA: W.B. Saunders Co., 1983. 745].

Once absorbed into the body, cyanide can form complexes with heavy metal ions. /Cyanide/ (NIOSH; Criteria Document: Hydrogen Cyanide and Cyanide Salts p.45 (1976) DHEW Pub. NIOSH 77-108].

Liquid hydrogen cyanide ran over the bare hand of a worker wearing a fresh air respirator. Cyanide inhalation was prevented, but the worker collapsed into deep unconsciousness within five minutes, suggesting significant percutaneous absorption. /Liquid hydrogen cyanide/ (Potter AL; Br J Ind Med 7: 125 (1950) as cited in USEPA; Ambient Water Quality Criteria Doc: Cyanides p.C-8 (1980) EPA 440/5-80-037].

## Laboratory and/or Field Analyses:

Determination of cyanide is (often) by volumetric titration or colorimetry [893]. There is general agreement that total cyanide concentrations in water in most cases will overestimate the actual cyanide toxicity to aquatic organisms, and that the analytically determined HCN concentration in cyanide-polluted waters is considered to be the most reliable index of toxicity [517].

Many methods have been used to monitor for cyanide [755,861].

EPA methods recommended depend on the application: whether for drinking water [1008 and 40 CFR Part 141], NPDES discharge permits [40 CFR 136], CERCLA [861] or RCRA [861].

Low concentration criteria or benchmarks may require relatively rigorous methods. Detection limits should be no higher than comparison benchmarks or criteria for various media (water, sediments, soil, tissues, etc, see sections above (Roy Irwin, National Park Service, Personal Communication, 1996).

Detection levels:

Solids: As low as 0.1 ppm for free cyanide in food or other solids [755].

Water: EPA method detection limits for cyanide in water can be as low as 0.005~mg/L and the drinking water MCL is 0.2~mg/L (40 CFR Part 141.23, part of the Drinking Water Regulations). Other detection levels which have been used: 0.1~ppm for either free cyanide or total cyanide in water [755].

Cyanide is a possible lab contaminant, as it is used in many lab methods, including the methods for analyzing several metals, chloride(s), and phenols in water [861].

Inorganic cyanides in water can be present both as complexed and free cyanide. Cyanide in water is usually determined in three different forms: free cyanide, cyanide amenable to chlorination, and total cyanide. Free cyanides such as sodium cyanide, potassium cyanide, and hydrogen cyanide are readily ionized to the cyanide ion under the conditions used in most common analytical techniques. Methods for determining cyanide amenable to chlorination measure simple metal cyanides and most complex cyanides with the exception of iron cyanides. Total cyanide is a measure of all cyanides including iron cyanide complexes [755].

It is important to understand that cyanide data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather The trend in quality assurance seemed to be for than better. various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bioconcentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods.

Analytical methods for determining free and bound cyanide and cyanogenic compounds in biological materials are under revision. Current methods include chromatography, enzymic postcolumn cleavage, electrochemical detection, and ultraviolet, infrared, proton, and carbon-13 nuclear magnetic resonance spectroscopies. Proposed newer analytical methodologies include chemiluminescence, deproteinization techniques, thin film dissociation coupled with preferential ultraviolet irradiation, differential polarography, and modified spectrophotometric, colorometric, and ion chromatographic determinations. Analysis of cyanide and cytochrome oxidase is usually conducted with samples of whole blood, serum, plasma, brain, or ventricular myocardium tissues. Samples should be obtained as soon as possible after cyanide exposure and analyzed immediately, otherwise erroneous analytical values will result. Brain and liver are recommended for cyanide analysis if removed and analyzed within a week. measurements are further confounded by the presence of various antidotal agents; by various tissue preservatives, such as formaldoxime and sodium fluoride; and by the spontaneous postmortem production of cyanide in various tissues (e.g., sterile blood, brain, liver, kidney, uterus, intestines) over time in cases of noncyanide death [517].

EPA 1996 Integrated Risk Information System (IRIS) Database Information on drinking water methods free cyanide, CAS number 57-12-5 [893]:

### Monitoring Requirements

Ground water systems every 3 years; surface water systems annually; will allow monitoring at up to 10-year intervals after the system completes 3 rounds of sampling at <50% of the MCL.

# Analytical Methods

Distillation, titrimetric (EPA 335.2; ASTM D-2036-82A; SM 412C; USGS I-3300-84); distillation, automated spectrometric (EPA 335.3; ASTM D-2036-82A; SM 412D): PQL= 0.2 mg/L.

Descriptions of Specific Lab Methods (no endorsement implied, check detection limits and other quality factors before using):

EPA - OSW 9010A A Total & Amen Cyanides - Color [861]. 1 SW-846 COLOR mg/L RNGE Method 9010A "Total and Amenable Cyanide" The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scubber containing sodium hydroxide solution [861]. The cyanide in the absorbing solution is then determined colorimetrically or titrametrically [861]. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNC1) by reaction of cyanide with chloramine-T at a pH less than 8 [861]. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent and CNCl [861]. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards [861]. The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator [861].

EPA - OSW 9010A B Total & Amen Cyanides - Titr [861]. TITR mg/L RNGE Method 9010A "Total and 1 SW-846 Amenable Cyanide" The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scubber containing sodium hydroxide solution [861]. The cyanide in the absorbing solution is then determined colorimetrically titrametrically [861]. In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNC1) by reaction of cyanide with chloramine-T at a pH less than 8 [861]. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent and CNCl [861]. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards [861]. The titration measurement uses a standard soltion of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator [861].

EPA - OSW 9012A Total & Amenable Cyanides 1 SW-846 COLOR ug/L Method 9012A "Total and Amenable Cyanide (Colorimetric, Automated UV)" The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution [861]. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry [861]. In the colorimetric measurement, cyanide is converted to cyanogen chloride (CNC1) by reaction with chloramine-T at

a pH less than 8 without hydrolyzing to the cyanate [861]. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent [861]. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity [861].

EPA - EMSLC 335.1 Cyanides 1 MCAWW SPECTR mg/L Cyanides, Amenable to Chlorination (Titrimetric; TITR Spectrophotometric) " A portion of the sample is chlorinated at a pH greater than 11 to decompose the Cyanide levels in chlorinated and cyanide [861]. unchlorinated aliquots are determined by the method for Cyanide, Total (Method 335.2) [861]. Cyanides amenable to chlorination are then calculated by difference [861]. titration procedure is used for measuring concentrations of cyanide exceeding 1 mg/L after removal of cyanides amenable to chlorination [861]. Below this level the colorimetric determination is used [861].

EPA - EMSLC 335.2 Cyanide - Titrimetric Cyanide, Total (Titrimetric; SPECTR mg/L EDL Spectrophotometric) TITR The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of reflux-distillation and absorbed in a scrubber containing sodium hydroxide solution [861]. The cyanide ion in the absorbed solution is then determined by volumetric titration or colorimetrically [861]. In the colorimetric measurement, the cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate [861]. After the reaction is complete, color is formed on the addition of pyridine-pyrazolone or pyridine-barbituric acid reagent [861]. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridinebarbituric acid [861]. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards [861]. titrimetric measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of silver sensitive indicator [861].

EPA - EMSLC 335.3 Cyanide - Colorimetric 1 MCAWW COLOR ug/L RNGE Cyanide, Total (Colorimetric, Automated UV)" Cyanide [as hydrocyanic acid (HCN)] is released from cyanide complexes by means of UV digestion and distillation [861]. Cyanides are converted to cyanogen chloride by reactions with chloramine-T which subsequently reacts with pyridine and barbituric acid to give a red-colored complex [861].

EPA - CLP ILM01 W Inorganics - Water 24 COLOR ug/L CRQL "Inorganics Analysis, Multi-Media, Multi- CVAA

Concentration"; USEPA Contract Laboratory Program, GFAA Statement of Work, Document Number IHCO1.2, U.S [861]. ICP Environmental Protection Agency, Washington, D.C., 20460 [861]. Methods are included for the analysis of 23 metals, cyanide, and percent solids [861]. Metals analysis is performed using inductively coupled plasmaatomic emission spectroscopy (ICP), furnace technique atomic absorption spectroscopy (GFAA), flame technique atomic absorption spectroscopy (FLAA), or cold vapor atomic absorption spectroscopy (CVAA) (for mercury) [861]. Cyanide is determined either by volumetric titration or colorimetrically [861]. The percent solids are determined gravimetrically [861].

EPA - CLP ILM01 S Inorganics - Soil 24 ug/kg CRQL "Inorganics Analysis, Multi-Media, Multi-CVAA Concentration"; USEPA Contract Laboratory Program, GFAA Statement of Work, Document Number IHC01.2, U.S. [861]. ICP Environmental Protection Agency, Washington, D.C., 20460 [861]. Methods are included for the analysis of 23 metals, cyanide, and percent solids [861]. Metals analysis is performed using inductively coupled plasmaatomic emission spectroscopy (ICP), furnace technique atomic absorption spectroscopy (GFAA), flame technique atomic absorption spectroscopy (FLAA), or cold vapor atomic absorption spectroscopy (CVAA) (for mercury) Cyanide is determined either by volumetric [861]. titration or colorimetrically [861]. The percent solids are determined gravimetrically [861].

APHA 4500-CN C Cyanide in Water 1 STD\_METHODS POTENT mg/L "4500-CN Cyanide" SPECTR TITR 4500-[861]. Total Cyanide after Distillation: Pretreatment depends upon sample composition (see Method 4500-CN B) [861]. Hydrogen cyanide (HCN) is liberated from an acidified sample by distillation and purging with air [861]. The HCN gas is collected by passing it through a sodium hydroxide (NaOH) solution [861]. Cyanide concentration in the solution is determined titrimetric, colorimetric, or potentiometric procedures [861].

4500-CN Cyanide in Water - Titrimetric APHA D STD\_METHODS TITR mg/L "4500-CN Cyanide" D [861]. Titrimetric Method: Cyanide in the NaOH distillate is titrated with silver nitrate to form a soluble silver cyanide complex [861]. The indicator changes color when all of the cyanide is complexed [861]. Cyanide concentration is based on the amount of titrant used to produce the color change [861]. If cyanide concentration is below 1 mg/L, colorimetric or potentiometric methods should be used [861].

STD\_METHODS COLOR mg/L "4500-CN Cyanide" 4500-CN E [861]. Colorimetric Method: Cyanide in the NaOH distillate is converted to CNCl by reaction with chloramine-T [861]. Pyridine-barbituric acid is added to CNCl, forming a red-blue dye which is measured at 578 nm [861].

APHA 4500-CN F Cyanide in Water - Ion Select [861]. 1 STD\_METHODS ISE-CN mg/L RNGE "4500-CN Cyanide" 4500-CN F [861]. Cyanide-Selective Electrode Method: Cyanide in the NaOH distillate can be determined with a cyanide selective electrode in combination with a double-junction reference electrode and a pH meter having an expanded milivolt scale [861].

APHA 4500-CN G Cyanides Amenable to Chlorinate 1 STD\_METHODS COLOR mg/L RNGE "4500-CN Cyanide" ISE-CN TITR 4500-CN G [861]. Cyanides Amenable to Chlorination after Distillation: (Dissociable cyanide content) [861]. A volume of sample is chlorinated to decompose the cyanides [861]. The chlorinated sample and a volume of untreated sample are distilled by the procedure in Method 4500-CN C [861]. The difference in concentrations found in the two samples represents cyanides amenable to chlorination [861].

J Cyanogen Chloride 1 STD\_METHODS APHA 4500-CN SPECTR mg/L "4500-CN Cyanogen Chloride" 4500-CN J [861]. Cyanogen Chloride: Add a portion of unstabilized sample, diluted if necessary, to contain 0.2 - 6 ug of CN-/40 mL to a beaker [861]. Add phosphate buffer to a pH of 6.5 (pH 6.0 - 6.6) [861]. Record exact volume of phosphate buffer required [861]. Prepare a second samle and add to a 50 mL volumetri flask [861]. Add phosphate buffer in the previously established volume [861]. Add 5 mL pyridine-barbituric acid solution [861]. Dilute to mark with distilled water and mix well by inversion [861]. Allow 8 min for color development [861]. Measure absorbance at 578 nm within 8 - 15 min from the addition of the pyridine-barbituric acid reagent [861]. Determine CNCl as CN- [861].

ASTM D2036 A Cyanides in Water - Colorimet [861]. 1 ASTM\_11\_02 SPECTR mg/L RNGE "Standard Test Methods for Cyanides in Water" Four test methods are provided [861]. The cyanide as hydrocyanic acid (HCN) is released from compounds by means of reflux distillation and absorbed in sodium hydroxide solution [861]. The conditions used for the distillation distinguish the type of cyanide [861]. The sodium cyanide in the absorbing solution can be determined colorimetrically, by titration or by selective ion electrode [861].

ASTM\_11\_02 TITR mg/L RNGE "Standard Test Methods for Cyanides in Water" Four test methods are provided [861]. The cyanide as hydrocyanic acid (HCN) is released from compounds by means of reflux distillation and absorbed in sodium hydroxide solution [861]. The conditions used for the distillation distinguish the type of cyanide [861]. The sodium cyanide in the absorbing solution can be determined colorimetrically, by titration or by selective ion electrode [861].

ASTM D2036 C Cyanides in Water - Ion Select [861]. 1 ASTM\_11\_02 ISE-CN mg/L RNGE "Standard Test Methods for Cyanides in Water" Four test methods are provided [861]. The cyanide as hydrocyanic acid (HCN) is released from compounds by means of reflux distillation and absorbed in sodium hydroxide solution [861]. The conditions used for the distillation distinguish the type of cyanide [861]. The sodium cyanide in the absorbing solution can be determined colorimetrically, by titration or by selective ion electrode [861].

ASTM D2036 D Cyanides without Distillation 1 ASTM\_11\_02 SPECTR mg/L RNGE "Cyanides Amenable to Chlorination Without Distillation, Short-cut Method" This test method covers the determination of the free CN-and Cn- complexes that are amenable to chlorination in water [861]. The procedure does not measure cyanates nor iron cyanide complexes [861]. I does, however, determine cyanogen chloride and thiocyanate [861].

1 ASTM\_11\_02 ASTM D4282 Free Cyanide in Water SPECTR uq/L RNGE "Standard Test Method for Determination of Free Cyanide in Water and Wastewater by Microdiffusion" This test method covers the determination of free cyanides in waters and wastewaters [861]. Free cyanide is defined as the cyanide which diffuses as cyanide at room temperature from a solution The reactions are carried out in a at pH 6 [861]. microdiffusion cell [861]. The sample is treated with cadmium ion to precipitate the hexacyanoferrates, and the sample is buffered at pH 6 and allowed to stand for 4 h [861]. The HCN diffuses into sodium hydroxide solution [861]. An aliquot of the sodium hydroxide solution is treated with chloramine-T, and the cyanogen chloride formed is reacted with barbituric acid in pyridine [861]. The absorbance of the color formed is measured using a spectrophotometer at a wavelength of 580 nm [861].

ASTM D4374 Cyanide in Water 1 ASTM\_11\_02 AUTO ug/L LLD "Standard Test Methods for Cyanide in Water-Automated Methods for Total Cyanide and Dissociable Cyanide" Some automated continous flow modules are used in addition to the newly developed on-line Thin Film Distillation and Ultraviolet Irradiation [861]. Three

factors control the separation of cyanides from the samples, namely (a) acidification, (b) air stripping, and (c) thin film distillation [861]. Acidification is made to pH < 1, but the sample exposure to heat treatment in the continuous thin film distillation is very short (few seconds) [861]. Thus the liberation of HCN is only from the free cyanides and the weak cyanide complexes, that is, the dissociable cyanides [861]. For total cyanides, the breakdown of the strong cyanide complexes, prior to thin film distillation, is achieved by UV irradiation [861]. Absoption of the liberated HCN gas is carried out using a glass coil and 0.02 M NaOH solution [861]. Colorimetric determination of the recovered cyanides is made by pyridine-barbituric acid reagent [861].

ASTM D5049 Α Cyanides in Waste - Chloramine ASTM 11 02 COLOR "Standard Test Methods for the Screening of Cyanides in Waste" Four test methods are provided [861]. They are applicable to the screening of cyanides in waste liquids, sludges, semisolids, and solids [861]. The test methods are designed and intended preliminary test to complement the sophisticated quantitative analytical techniques that may be used to determine CN concentration [861]. Test Method A, Chloramine-T Method: the presence of cyanides can be observed when cyanides react with chloramine-T reagent at pH 8 to form cyanogen chloride [861]. The addition of barbituric acid to cyanogen chloride gives intensive red color [861]. This test method will indicate cyanides amenable to chlorination [861].

D5049 Cyanides in Waste - Prussian ASTM В ASTM\_11\_02 COLOR "Standard Test Methods for the Screening of Cyanides in Waste" Four test methods are provided [861]. They are applicable to the screening of cyanides in waste liquids, sludges, semisolids, and solids [861]. The test methods are designed and intended preliminary test to complement the sophisticated quantitative analytical techniques that may be used to determine CN concentration [861]. Test Method B, Prussian Blue Method: the pH of a sample is adjusted to pH 12 with NaOH and subsequently, solutions of ferrous sulfate and ferric chloride are added [861]. addition of concentrated sulfuric acid in the presence of cyanides, a deep blue color (Prussian blue) is produced [861]. This test method will indicate the presence of free cyanide and many of the complex cyanides [861].

ASTM D5049 C Cyanides in Waste - Cyantesmo 1 ASTM\_11\_02 WET "Standard Test Methods for the Screening of Cyanides in Waste" Four test methods are provided [861]. They are applicable to the screening of cyanides in waste liquids, sludges, semisolids, and solids [861]. The test methods are designed and intended

as a preliminary test to complement the more sophisticated quantitative analytical techniques that may be used to determine CN concentration [861]. Test Method C, Cyantesmo Paper Method: a portion of the sample is acidified in a flask or test tube releasing the simple hydrogen cyanide gas from cyanides [861]. The presence of hydrogen cyanide gas is indicated by a color change in the cyanide screening paper that is held just above the solution [861]. This test method will indicate dissociable cyanide that could readily evolve hydrogen cyanide gas [861].

ASTM D5049 Cyanides in Waste - Gas Tube D "Standard Test Methods for the ASTM 11 02 TGVTUB Screening of Cyanides in Waste" Four test methods are provided [861]. They are applicable to the screening of cyanides in waste liquids, sludges, semisolids, and solids [861]. The test methods are designed and intended a preliminary test to complement the sophisticated quantitative analytical techniques that may be used to determine CN concentration [861]. Test Method D, Gas Detector Tube Method: a portion of the sample is acidified in a beaker to release cyanide as hydrogen The gas is funneled through a cyanide gas [861]. detector tube creating a color stain in the tube in proportion to the concnetration of cyanide gas in the vapor [861]. A definite color change in the detector tube indicates a positive presence of cyanide [861]. This test method will indicate dissociable cyanide that could readily evolve into hydrogen cyanide gas [861].

USGS I1300 S Cyanide - Soil, Spectrometric 1 USGS\_METHODS SPECTR mg/kg DL "Cyanide, Colorimetric, Pyridine-Pyrazolone" This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye [861]. The method detects only simple cyanides; therefore, any complex cyanide must be broken down [861]. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure [861]. The distillation also removes certain interferences from water samples [861].

USGS I1300 W Cyanide - Water, Colorimetric 1 USGS\_METHODS SPECTR mg/L DL "Cyanide, Colorimetric, Pyridine-Pyrazolone" This method is based on the chlorination of cyanide and the subsequent reaction of the product with a mixed solution of pyridine-pyrazolone to form a stable complex dye [861]. The method detects only simple cyanides; therefore, any complex cyanide must be broken down [861]. The decomposition of complex cyanides is accomplished by an acid reflux and distillation prior to the colorimetric procedure [861].

The distillation also removes certain interferences from water samples [861].

USGS I2302 S Cyanide - Barbituric Acid 1 USGS\_METHODS AUTO mg/kg DL "Cyanide, Colorimetric, Barbituric Acid, Automated-Segmented Flow" This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent [861]. This method detects simple cyanides only, therefore, and complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure [861]. The distillation step also removes certain interferences [861].

USGS I2302 W Cyanide - Barbituric Acid 1 USGS\_METHODS AUTO mg/L DL "Cyanide, Colorimetric, Barbituric Acid, Automated-Segmented Flow" This method is based on the chlorination of cyanide with chloramine-T and on the subsequent reaction with a pyridine-barbituric acid reagent [861]. This method detects simple cyanides only, therefore, and complex cyanides must first be broken down by passing the acidified sample solution through an ultraviolet digestion-distillation procedure [861]. The distillation step also removes certain interferences [861].