

Cyanide Discharges in the Petroleum Industry: Sources and Analysis

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Regulatory and Scientific Affairs Department

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Abstract

When water quality criteria for cyanide are incorporated in NPDES permits, the resulting water quality-based effluent limits may be very low (e.g., 5-20 µg/L). This is especially true when a discharge is to a surface water body with very little allowable effluent dilution (i.e., a limited mixing zone). Because both industrial and municipal dischargers have been issued NPDES permits with these low effluent limits, there has been considerable interest in the reliability of the available test methods at these low concentrations. This report provides guidance on the measurement, as well as the presence and environmental fate, of cyanide compounds and related chemical species in petroleum industry wastewater effluents. The report provides technical information to assist NPDES permittees in negotiating site-specific water quality-based effluent limits for cyanide. The report also provides permittees with guidance on the sampling and analytical methods that must be used to assure that cyanide data are as reliable as practical, given the limitations of the analytical methods. Addressed within the report are analytical methods frequently specified for measuring total cyanide and simple cyanides, including available cyanide, weak acid dissociable cyanide, and free cyanide. All of the analytical methods for cyanide are subject to matrix interferences when wastewater and surface water samples are analyzed, and method performance testing is recommended for cyanide concentrations below 30-50 µg/L.

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Executive Summary

The chemical functional group cyanide (CN) is found on a number of inorganic and organic compounds. Chemicals containing CN have considerable environmental importance because when CN is present as “free” cyanide — hydrocyanic acid (HCN) and the CN^- anion — it is highly toxic to many life forms. Cyanide complexes with alkali metals (sodium, potassium), and certain metals such as cadmium and zinc, that dissociate readily in water and exert toxicity equivalent to free cyanide. Cyanide present in stable complexes with metals such as iron and cobalt is not typically toxic in wastewater and surface water. Organic cyanides (nitriles) are also generally less toxic to aquatic life than simple cyanides.

The U.S. Environmental Protection Agency (EPA) has published water quality criteria for free cyanide. These criteria are very low, on the order of 1-20 $\mu\text{g/L}$. Most states have adopted the EPA water quality criteria as water quality standards and may apply them as either “free” cyanide or “total” cyanide. Free cyanide criteria expressed as total cyanide are very conservative because of the assumption that stable metal-cyanide complexes will exert toxicity to aquatic life that is equivalent to free cyanide. The stable metal-cyanide complexes can dissociate to free cyanide when exposed to ultraviolet light. Because ultraviolet light is attenuated rapidly by suspended material in an ambient surface water column and by the water itself, however, the rate at which free cyanide is released from metal-cyanide complexes will generally be so low that there is a negligible potential for free cyanide to reach toxic concentrations.

When water quality criteria for cyanide are incorporated in NPDES permits, the resulting water quality-based effluent limits may be very low (e.g., 5-20 $\mu\text{g/L}$). This is especially true when a discharge is to a surface water body with very little allowable effluent dilution (i.e., a limited mixing zone).

Wastewaters containing cyanide are generated only in the refining sector of the petroleum industry, and then only in a few processes. The sour water streams generated by thermal cracking and visbreaking, catalytic cracking, hydrocracking, delayed coking, and fluidized bed coking are the refinery wastewater streams that will contain potentially significant amounts of cyanide and thiocyanates. Cyanides are formed in these processes because they operate in the absence of oxygen (i.e., in a reducing environment), and the nitrogen present in the hydrocarbon streams will react at the heat and pressure of these processes to form cyanide. Historically, the amount of cyanides in these wastewater streams has not been considered of regulatory concern because the typical refinery treatment processes (oil and solids separation, biological treatment) remove them efficiently. Refiners have also found that adding polysulfides to thermal cracking wastewaters will efficiently convert simple cyanides to thiocyanates, which will not convert back to cyanide during wastewater treatment. This has proven to be an effective method for complying with cyanide limits for most petroleum refineries. However, because the water quality-based effluent limits for cyanides may be very low for some refineries (i.e., $< 20 \mu\text{g/L}$), the ability of the available analytical methods to demonstrate compliance with NPDES permit limits is a continuing problem.

Problems with complying with very low water quality-based limits for cyanide are not confined to petroleum refineries. Municipalities and a number of other industrial categories (e.g., organic

chemicals, inorganic chemicals, iron and steel) have also struggled with very low cyanide limits and analytical problems.

There are analytical methods available for measuring the forms of cyanide compounds that are important in wastewater discharges and are regulated by water quality standards. These include methods for: (1) total cyanide [CN(T)], which includes simple cyanide and the stable metal-cyanide complexes; (2) simple cyanides, which include HCN and CN^- , the alkali metal cyanide compounds, and the readily dissociable metal cyanide complexes; (3) thiocyanate (SCN^-); (4) cyanates (OCN^-); and cyanogen chloride (CNCl). The simple cyanides, the forms of cyanide that most closely represent the free cyanide used in the EPA and state water quality criteria, can be measured using several different analytical methods. These include: (1) available cyanide [CN(A)], as defined in EPA's analytical methods for NPDES permits (40 CFR 136); (2) weak acid dissociable cyanide [CN(W)], as defined in *Standard Methods for the Analysis of Water and Wastewater* (APHA, 1999); and free cyanide [CN(F)], as defined by [ASTM \(Method D 4282-02\)](#).

Because both industrial and municipal dischargers have been issued NPDES permits with water quality-based effluent limits for cyanide that are often very low (e.g., 5-20 $\mu\text{g/L}$), there has been considerable interest in the reliability of the available test methods at these low concentrations. This interest has resulted in several research projects in the last 10 years, including a \$1.5 million project sponsored by the Water Environment Research Federation (WERF), to evaluate the capabilities of the existing analytical methods for cyanide and to develop new methods and improvements to existing methods.

The method for available cyanide that has historically been the most widely used, cyanide available to chlorination (EPA Method 335.1), has been repeatedly demonstrated to be subject to so many matrix interferences¹ that it cannot be recommended for general use for NPDES permit compliance testing of petroleum industry wastewaters, unless site-specific performance tests indicate that it gives reliable results at permit limit levels. Method OIA-1677 for CN(A), which was approved by EPA for NPDES compliance testing in 2001, has been demonstrated to provide acceptable performance for testing wastewater samples at cyanide concentrations as low as 5 $\mu\text{g/L}$. The analytical methods for CN(W) and CN(F) have also been demonstrated to achieve acceptable performance on wastewater samples with cyanide concentrations as low as 5 $\mu\text{g/L}$. Because the CN(W) and CN(F) methods are not approved at 40 CFR 136, a permittee must seek state, and possibly EPA, approval to use them for NPDES compliance testing. However, this approval is usually not difficult to obtain because most permitting authorities are aware of the limitations of the approved tests for cyanide and some states accept the use of the CN(W) method for compliance testing without any site-specific demonstration.

All of the analytical methods for cyanide are subject to matrix interferences when wastewater and surface water samples are analyzed. These interferences are most pronounced at the low cyanide concentrations typical of water quality-based effluent limits found in NPDES permits. In addition, because many interferences in these methods are positive (i.e., report greater than the true amounts of cyanide present in the sample), there is a significant risk for some dischargers that they will report an exceedance of a cyanide limit when they are actually in compliance.

¹ The most common interference from a petroleum industry standpoint is that some unidentifiable compounds in the petroleum refinery wastewaters react with chlorine and generate compounds that are measured as CN by the analytical method.

Sulfides and nitrites/nitrates, which can be found in biologically treated petroleum refining effluents, can cause significant positive interferences in the analytical methods for cyanide. Thus, permittees that must comply with such limits should always consider conducting sufficient performance testing on their specific effluent matrix to assure that the results that they are obtaining from the laboratory are valid.

There are corrective actions that can be taken during sample collection and preparation for analysis, and these are described in this report. The corrective actions include:

- Immediate addition² of sodium hydroxide to raise the sample pH to >12.0;
- Immediate addition of sulfamic acid if the sample may contain nitrites and/or nitrates (to reduce the nitrites/nitrates to nitrogen gas);
- Refrigeration of the sample at 4 °C until analysis.
- Before analysis, if the sample contains sulfide, add lead acetate or lead carbonate to precipitate the sulfide.

These actions will minimize interferences, but cannot guarantee accurate and precise measurements at low cyanide concentrations in all effluent matrices and surface waters. Therefore, it is prudent to conduct matrix-specific performance testing, as recommended above, if a permittee must comply with permit limits based on cyanide concentrations below 30-50 µg/L.

² This means in the field, when the sample is collected.

Glossary of Terms

Amenable cyanide	Cyanide in a water or waste sample that can be oxidized by free chlorine. Also known as cyanide amenable to chlorination and abbreviated as CN(A), this is the pollutant parameter that is measured by a specific analytical method and the result is intended to represent free cyanide plus simple cyanides.
Complexed cyanide	The cyanide anion associated that is with an alkali and a metal such as iron or cobalt. Potassium ferrocyanide is considered a complexed cyanide. Complexed cyanide compounds are usually very stable in water (i.e., they do not readily dissociate to HCN).
Cyanate	An anion in which the carbon that is bonded to the nitrogen has a covalent bond to oxygen ($\text{-O-C}\equiv\text{N}^-$). This anion is correctly abbreviated as OCN^- , but some references abbreviate it as CNO^- .
Free cyanide	Unionized hydrocyanic acid (HCN) in aqueous solutions. HCN is the form of cyanide most toxic to aquatic life.
Fulminate	An anion in which oxygen is bonded to nitrogen, which in turn is bonded to carbon ($\text{-C}\equiv\text{N}^+\text{-O}^-$). Abbreviated as CNO.
Isocyanate	The functional group -N=C=O covalently bonded to a hydrocarbon, i.e., R-NCO.
Nitrile	The functional group $\text{-C}\equiv\text{N}$ covalently bonded to a hydrocarbon, i.e., R-CN.
Thiocyanate	An anion in which the carbon that is bonded to nitrogen is also bonded to sulfur ($\text{-S-C}\equiv\text{N}^-$). Abbreviated as SCN^- .
Simple cyanide	The cyanide anion associated with an alkali or metal. Examples are potassium cyanide (KCN) and cuprous cyanide (CuCN). Simple cyanides readily dissociate in water to HCN because HCN is a weak acid ($\text{pK} = 9.2$).
Weak acid dissociable cyanide	Cyanide liberated from aqueous solution with the pH adjusted to 4.5-6.0 Standard Units (SU) by an acetate buffer. Abbreviated as CN(W), this is a pollutant parameter that is intended to measure only the simple and free cyanides in the aqueous sample. Zinc acetate is added to the sample to precipitate out iron cyanides and ensure they are not measured as CN(W).

The American Petroleum Institute's (API) Clean Water Issues Task Force (CWITF) commissioned this report to provide information and guidance to its members on the importance, presence, environmental fate, and analytical methods for cyanide compounds and related chemical species that may be found in petroleum industry wastewater effluents. A principle objective of this report is to provide technical information that will assist NPDES permittees in negotiating site-specific water quality-based effluent limits. The report also provides permittees with guidance on the sampling and analytical methods that must be used to assure that cyanide data are as reliable as practical, given the limitations of the analytical methods.

There are currently no national effluent limitations guidelines for cyanide and related chemicals that are applicable to petroleum industry discharges. However, the U.S. Environmental Protection Agency (EPA) has adopted water quality criteria for cyanide (EPA, 1985) under the authority of Section 304(a) of the Clean Water Act (CWA). All of the states and territories have used EPA's criteria, either directly or with modifications, to adopt water quality standards for cyanide under the authority of Section 303(c) of the CWA. Because the water quality standards for cyanide are uniformly very low, and because certain petroleum industry wastewaters contain cyanides, it is important for API member companies to have information resources that will: (1) assist them in participating in future regulation development by the states; (2) provide technical support for the development of NPDES permit limits, and (3) provide technical support for determining the levels of treatment required to achieve water quality-based effluent limits (WQBELs) that may be included in NPDES permits. Also, although this study did not identify in any states any stream segments impaired by cyanide, there is always the possibility that such a identification could occur and that a total maximum daily load (TMDL) evaluation for cyanide would then be required. The information in this report will be helpful in such cases, if they were to occur.

Properties of Cyanides and Related Chemicals

The chemical functional group cyanide (CN) is found on a number of inorganic and organic compounds. Chemicals containing CN have considerable environmental importance because when CN is present as “free” cyanide (hydrocyanic acid (HCN) and the CN^- anion), it is highly toxic to many life forms.

There are several other functional groups that contain the CN structure, but that generally are much less toxic than CN. These include the thiocyanate (SCN^-) group, the cyanate group (OCN^-), organic nitriles, and the selenocyanate group (SeCN^-). Because these forms are found in certain petroleum wastes and as degradation products of free cyanide, they are also discussed in this section.

Cyanide

In water CN can be present as HCN, CN^- , simple cyanides (i.e., the CN group and an alkali or metal such as NaCN, KCN, CuCN, CdCN), and metallocyanide complexes (alkali-metal cyanides such as potassium ferrocyanide)(APHA, 1999). The simple alkali cyanides dissociate readily in water. Because the pK_a of HCN is approximately 9.2, in most natural surface waters, where the pH range is most typically between 6.5 and 8.5, the predominant species of CN from the dissociation of simple alkali cyanides is HCN, the most toxic form. EPA’s national surface water quality criteria are based on the concentration of free CN ($\text{HCN} + \text{CN}^-$) in water (EPA, 1985).

The simple metallocyanides (not the complexes) have a wide range of stabilities in water. Zinc and cadmium cyanides dissociate rapidly and nearly completely in dilute solutions (EPA, 1985). Dissociation of copper, nickel, and silver cyanides in dilute aqueous solution is pH-dependent and much less complete than that of the zinc and cadmium complexes (APHA, 1999).

Iron cyanide complexes are very stable and thus have a low potential to cause aquatic toxicity due to CN release. However, all of the more stable metallocyanide compounds can be broken down by exposure to ultraviolet light and therefore, in direct sunlight and clear water, theoretically can release sufficient HCN and CN^- to be a potential cause of aquatic toxicity (EPA, 1985). As a practical matter, ultraviolet light attenuation due to water and to particulate matter in the water column makes it very unlikely that this mechanism will release toxic quantities of HCN in ambient surface water. Because of this, water quality-based effluent limits for

cyanide that are applied in NPDES permits are based on a measure of free cyanide (e.g., CN(A), CN(W)).

Free cyanide in surface waters is highly toxic to a number of fresh water fish species including trout, salmon, bluegill, and fathead minnows (EPA, 1985). Fresh water invertebrate animals are generally less sensitive to CN than fishes.

Certain marine species are even more sensitive to CN than the fresh water fishes. EPA's water quality criteria database for marine species is much smaller than its fresh water species database, but shows that free CN is highly toxic to fishes, copepods, and at least one species of crab.

Related Chemicals

Thiocyanates (SCN^-) are much less toxic to aquatic life than free CN and are biodegradable. Biodegradation of thiocyanate results in the formation of ammonia (APHA, 1999). Thiocyanate cannot be naturally transformed to free CN in surface waters. However, chlorination of aqueous solutions of thiocyanate will form cyanogen chloride (CNCl), a chemical that is potentially more toxic than free CN.

The cyanate anion (OCN^-) is an oxidation product of CN. It has a much lower toxicity than free HCN. There is no known natural reduction reaction that can change OCN^- to CN (APHA, 1999).

Organic chemicals that contain the CN functional group are called nitriles. Acetonitrile and acrylonitrile are two common examples of this class of organic compound. Nitriles do not ionize to free CN in water.

Petroleum Industry Sources

Wastewaters containing cyanide are generated only in the refining sector of the petroleum industry, and then only in a few processes. Cyanides are formed when carbon and nitrogen combine at high temperatures and in the absence of oxygen. In petroleum refining, this effectively limits the potential for formation of cyanides and thiocyanates to the cracking and coking processes (EPA, 1995; Kunz, R.G., Casey, J.P. and Huff, J.E., 1978).

The sour water streams generated by thermal cracking and visbreaking, catalytic cracking, hydrocracking, delayed coking, and fluid coking are the refinery wastewater streams that will contain potentially significant amounts of cyanide and thiocyanates. Historically, the amount of cyanides in these

wastewater streams has not been considered of regulatory concern because the typical refinery treatment processes (oil and solids separation, biological treatment) remove them efficiently. Cyanides and thiocyanates were not identified by EPA as pollutants requiring national regulation by the effluent limitations guidelines and standards (40 CFR 419) because they are effectively controlled by the best practicable control technology (BPT) and best available technology (BAT) that is employed by the petroleum refinery sector.

As states adopted and implemented surface water quality standards, some refineries were given water quality-based NPDES permit limits for cyanide that were extremely low (e.g., in the 5 µg/L to 20 µg/L range) and were sometimes found to be problematic. Typically, these very stringent water quality-based effluent limits (WQBELs) for cyanide occur in cases where a state does not allow any mixing zone, or allows an extremely limited mixing zone, at the discharge point to the receiving water. As an example, in some western states the critical low flow in the river or stream to which a refinery discharges may be a small fraction of the refinery effluent flow, or sometimes even zero.

Refineries have responded to these very stringent permit limits by using various methods to enhance the destruction of cyanide in the process wastewaters. One of the most widely used practices is to inject polysulfide chemicals into the sour waters from the cracking and coking process to convert free cyanide and simple cyanides to thiocyanates. As discussed earlier, aqueous solutions of thiocyanate will not convert back to free cyanide in either wastewater treatment or the receiving water and therefore this conversion is equivalent to the removal of cyanide from the effluent.

Notwithstanding the efficiency of the cyanide treatment methods employed by refineries, continuous compliance with NPDES permit limits that are at or below 30-50 µg/L of free CN can be problematic, often because of the limitations of the analytical methods for free CN. Also, some states apply EPA's surface water criteria as total CN, which will measure metalocyanide complexes that are not biologically available.³ Because of these continuing difficulties with CN limit compliance that are experienced by some refineries, this report was prepared by API to provide members with technical information that will assist them in resolving analytical issues with CN limit compliance.

³ This is usually done because the state is concerned that the stable metal-cyanide complexes may dissociate in sunlight.

As discussed in the introduction, cyanides and related chemicals have long been known to be highly toxic to all forms of life. This is especially true for free CN in water, which can be toxic to a number of important aquatic life species at very low concentrations. Because of this toxicity, regulatory authorities have established water quality standards and effluent limits for cyanide compounds for many years. These standards and effluent limits are used to regulate the quantities of cyanide compounds that may be discharged to surface waters to assure that the indigenous aquatic life is protected and that there are no risks to human health.

The regulatory framework of the Clean Water Act (33 U.S.C.) requires EPA to develop water quality criteria that will be protective of the designated uses of surface waters. The water quality criteria adopted by EPA are used as guidance by the states, to which the CWA assigns the responsibility of adopting and implementing water quality standards. These state water quality standards are used to evaluate each point source discharge to waters of the state to assure that the designated uses of the receiving water will be achieved. If a pollutant (or pollutants) in a discharge is determined by the state to cause or contribute to an exceedance of the applicable water quality standard(s), then water quality-based effluent limits (WQBELs) will be established in the NPDES permit for the point source to assure that no exceedances of the water quality standard will occur.

The following sections describe the basis for EPA's water quality criteria and for each of the individual states' criteria.

EPA Water Quality Criteria

EPA's water quality criteria for cyanide are described in the criteria document (EPA, 1985). In the criteria document, EPA provides the database used to develop the criteria, the assumptions that it made in the criteria development process, its calculations, and the final criteria. Table 1 shows the EPA water quality criteria for cyanide. Note that EPA's adopted criteria are for *free cyanide* (HCN and CN⁻), the most toxic form of cyanide.

Table 1
EPA and State Water Quality Criteria
For Cyanide
(µg/L)

State	Aquatic Life Criteria				Human Health	
	Fresh Water		Marine Water		Drinking	Fish Consumption
	Acute	Chronic	Acute	Chronic		
California	22	5.2	1	1	700	220,000
Indiana ⁵	22	5.2	NA	NA	200	
Louisiana	45.9	9.4	1	NA	663.8	12,844
New Jersey	22	5.2	1	1	768	220,000
Pennsylvania ^{1,2}	22	5	NA	NA	700	NA
Texas ¹	45.8	10.7	5.6	5.6	200	NA
Washington ³	22	5.2	1 ⁴	NA		
EPA Criteria ¹	22	5.2	1	1	700	220,000

¹Criteria are identified as free cyanide

²In certain specified watersheds: free cyanide = 5 µg/L, total cyanide = 25 µg/L (acute/chronic not specified)

³Criteria are for weak acid dissociable cyanide

⁴Criteria for certain specified estuarine waters are 2.8 µg/L chronic and 9.1 µg/L acute (note: the text of the rule reverses these two criteria)

⁵Criteria are for free cyanide in Great Lakes basin waters and total cyanide for all watersheds that do not drain into the Great Lakes

Fresh Water Criteria

EPA's fresh water criteria are calculated from a database of acute toxicity to aquatic species and a second database of chronic toxicity data (EPA, 1985). The acute toxicity database consists of 15 genera of aquatic animals; 9 are fishes and 6 are invertebrates. EPA also evaluated toxicity data for aquatic plants, but these data were not used to develop the aquatic life criteria.

Within each genera that EPA used to develop the criteria there are typically multiple toxicity data sets. The acute toxicity data used by EPA to establish the acute criterion for CN are LC50 values⁴. Although not shown in the criteria document, the exposure times for these acute tests would be expected to be in the 24-hour to 96-hour range.

EPA's acute toxicity database (Tables 1 and 3, EPA, 1985) indicates that juvenile fish are the most sensitive fresh water aquatic species to free CN. Adults, embryos, and fry were less sensitive. In general, invertebrate species are less sensitive than fishes but *Daphnia sp.* and an amphipod, *Gammarus pseudolimnaeus*, showed comparable sensitivity to fish.

⁴ An LC50 value is the concentration of a chemical that is lethal to 50% of the organisms exposed in a toxicity test of a specified duration. LC50 values can be calculated from flow-through, static, and static renewal toxicity tests.