

Cyanide Discharges in the Petroleum Industry: Sources and Analysis

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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 (HCN + 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 metallocyanide 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.

Concentrations of free CN from 50 µg/L to 200 µg/L were shown to be rapidly lethal to juveniles of most of the sensitive fish species. Concentrations above 200 µg/L were rapidly lethal to juveniles of almost all species of fish.

The fresh water acute criterion of 22 µg/L is calculated from a final acute value (FAV) of 44.75 µg/L, which is based on rainbow trout. The criterion maximum concentration (CMC, which is the acute criterion shown in Table 1) is set at 22 µg/L, which is one-half of the FAV.⁵

The fresh water chronic criterion for free CN (the criterion continuous concentration or CCC) was calculated with data for four animals for which both acute and chronic toxicity test data were available. These species were brook trout, bluegill, fathead minnow and the amphipod *G. pseudolimnaeus*. The geometric mean of the acute to chronic ratios for these four species was 8.568. The final chronic criterion of 5.2 µg/L of free cyanide was calculated by dividing the final acute value (FAV) of 44.75 µg/L by the final acute to chronic ratio of 8.568.

Marine Water Criteria

The free CN acute aquatic life criterion for marine water that is shown in Table 1 was calculated from a database of five fish genera and five invertebrate genera (EPA, 1985). Unlike the fresh water species, the most sensitive organisms in the marine species database were the larvae of the rock crab (*Cancer irroratus*). The other invertebrate animals in this database were markedly less sensitive to free CN. The acute values for the fish species in this database ranged from 59 µg/L to 372 µg/L.

EPA calculated the FAV using the LC50 values for the four most sensitive species in the marine water database: mysid shrimp, Atlantic silverside, the copepod *A. clausi*, and the rock crab. The resulting FAV was 2.030 µg/L that becomes a CMC of 1.015 µg/L (which is rounded to 1 µg/L) when divided by the LC₅₀:CMC adjustment factor of 2 described earlier.

Chronic toxicity data for marine species were limited to two species, the mysid shrimp and sheepshead minnow. These two species also had acute toxicity data and EPA calculated the acute to chronic ratios as 1.621 and 8.306 for the mysid shrimp and sheepshead minnow, respectively (EPA, 1985). Rather than use these acute-chronic ratios to calculate a chronic criterion for

⁵ The CMC is calculated as one-half of the FAV because the FAV is an LC50 value and the division of the FAV by 2 is designed to assure that >95% of exposed animals will survive.

marine species, EPA elected to set the final chronic value for free CN at 1 µg/L, the same value as the acute criterion. It justified this decision on the basis that the acute criterion was based on the toxicity of free CN to rock crab larvae that, although not an endpoint for the chronic toxicity test, is a very sensitive life stage. It also stated that the 1 µg/L criterion is at equal to or less than 5/8th of a chronic criterion derived using the geometric mean acute to chronic ratio and the species mean acute values for all marine species in the database other than the rock crab.

EPA also had chronic toxicity data for the marine red macroalgae *Champia parvula* showing that growth and reproduction were adversely affected at free CN concentrations of 11 to 25 µg/L (EPA, 1985). Although these data were not used to establish the final chronic value free CN in marine waters, EPA stated that the toxicity data for this plant species lend credibility to its selection of the low chronic value of 1 µg/L.

State Water Quality Standards

As described earlier in this report, it is the states that adopt and implement water quality standards that are designed to protect all designated uses in specific surface waters of the state. EPA's national criteria are used as guidelines for state standards, but states may adopt alternative standards if they are scientifically justified.

This project reviewed the water quality standards of seven representative states with a significant amount of petroleum refining capacity. Table 1 shows the water quality standards for cyanide in these states.

States Using EPA Criteria

California, Indiana, and New Jersey have all adopted EPA's national water quality criteria for cyanide with no changes. Pennsylvania and Washington have adopted EPA's national criteria for most surface waters, but have different numerical cyanide standards for specifically designated surface waters.

One possible deficiency in a number of these state-adopted standards is that they do not identify the form of cyanide for application of the standard. One of the states reviewed, Indiana, adopted the EPA fresh water criteria for free cyanide but defines the regulated chemical as total cyanide. The CWA and EPA's water quality standards regulations (40 CFR 131) allow states to adopt more restrictive standards than the EPA criteria. The

decision by Indiana to regulate CN using the total CN analysis results in substantially more restrictive water quality standards than the EPA water quality criteria that are based on free CN.

Texas and Pennsylvania are the only states reviewed that explicitly identify the regulated form of CN as free CN. Washington identifies the regulated form of the chemical as weak acid dissociable CN, the analyte for one of the analytical methods used to measure free CN (See Chapter 5).

In those states with standards silent on the form of CN that is regulated but that have standards based on EPA's national criteria, it is justified to assume that free CN is the regulated pollutant. Unless a state has explicitly stated in its regulations that their cyanide standards apply to total cyanide (e.g., Indiana in Table 1), then its adoption of EPA's criteria without change is adoption of a free CN standard.

States With Criteria Different from EPA's

Two states, Louisiana and Texas, have fresh water quality criteria for cyanide that are substantially different from the EPA criteria. Although the fresh water standards of these two states differ slightly, both were derived in the same way using the procedures in EPA's *Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses* (Stephan, C.E., et.al., 1985). The two states removed the two most sensitive genera, *Salmo sp.* (rainbow trout and Atlantic salmon) and *Salvelinus fontinalis* (brook trout), from the cyanide toxicity database and recalculated the acute and chronic criteria using the EPA methodology. These two genera were removed from the database because they are coldwater fishes and there are no indigenous coldwater species in Louisiana and Texas.

Texas also recalculated the marine criteria for free CN using the same approach. It determined that rock crab was not indigenous to Texas waters and that there were insufficient data to document that indigenous warm water crab species were as sensitive to free cyanide as rock crab. It then recalculated the free CN criteria for marine species using EPA's methodology and the revised toxicity database.

Pennsylvania has cyanide criteria that differ from EPA's for certain surface waters in the Delaware River Basin. This is a consequence of its use of Delaware River Basin Commission (DRBC) water quality criteria for these streams. There are two criteria — one is for total cyanide and is 25 µg/L; the other is for free cyanide and is 5 µg/L, the same as the EPA CCC.

Washington has separate cyanide water quality criteria that apply to certain estuarine waters that are identified in the regulation. These numeric criteria are less restrictive than the EPA marine criteria. Both criteria are for weak acid dissociable cyanide. These modified estuarine criteria have a similar scientific basis as the Texas criteria — they are set to protect indigenous marine species and not be overprotective by including toxicity data for non-native species, i.e., the rock crab.

Summary of State Cyanide Criteria

The majority of states have adopted EPA's national water quality criteria for free CN. Three of the states reviewed, Louisiana, Texas, and Washington, evaluated the aquatic toxicity database that was used to calculate EPA's criteria and determined that species were used to calculate the national criteria that were not indigenous to the states' waters. Therefore they modified the database to represent only species native to the state. This resulted in state standards for free CN that are less restrictive than the national criteria.

It is reasonable to expect every state to review the aquatic life toxicity database that EPA uses to develop national water quality criteria and to adjust that database, as needed, so that it accurately represents native species. However, few states have historically performed such evaluations and it is common state practice to adopt EPA's criteria without change. In the case of the cyanide criteria, this approach has resulted in stringent cyanide criteria that may be unnecessary to protect indigenous aquatic life uses in many of the states. In states with no native coldwater fisheries that support salmon and/or trout, recalculation of the free cyanide criteria would result in fresh water standards similar to those adopted by Louisiana and Texas. Similar reevaluation of the marine and estuarine water quality criteria considering only those species indigenous to a state's waters could likewise result in an increased free CN standard similar to those adopted by Texas and Washington.

As described in the introduction, cyanides are formed in refinery processes that operate at high temperatures on petroleum feedstocks that contain nitrogen. At high temperatures, in the absence of oxygen, the nitrogen in the feedstocks will combine with carbon to generate the cyanide group. If hydrogen is present, such as in hydrocracking units, the formation of cyanide is reduced because ammonia is generated preferentially. Cyanide can also be formed in refinery processes by the breaking of the carbon-carbon bonds of nitrile compounds that may be present in crude petroleum.

Sources

Cracking and coking feedstocks contain nitrogen and sulfur in addition to hydrocarbons and trace amounts of other cations and anions that are naturally present in petroleum crudes. The amount of nitrogen in these feedstocks, and therefore the potential to generate cyanides in the cracking and coking processes, is dependent to some extent on the petroleum source (Engineering-Science, Inc., 1975). Some petroleum crudes, e.g, California crudes, contain high contents of nitrogen and therefore have a higher potential to generate cyanides in the cracking and coking processes. However, there are no data in the published technical literature that allow development of a quantitative correlation between crude petroleum nitrogen content and cyanide generation in cracking and coking processes.

When cyanide is generated in the refinery thermal processes it will react with available cations present in the hydrocarbon stream, because the cyanide group is anionic. The cyanide compounds partition from the hydrocarbon stream into water that is injected into the distillation column overhead gas stream from the thermal process to control corrosion (Kunz, R.G., Casey, J.P. and Huff, J.E., 1978). This water, which also contains high concentrations of hydrogen sulfide and ammonia and is called sour water in refinery terminology, is collected in accumulators and sent to treatment.

The available literature does not provide much data on the relative proportions of complex and free cyanide in refinery sour waters. Kunz, R.G., Casey, J.P. and Huff, J.E. (1978) cite a report that presented data from three Illinois refineries that reported long-term average percentages of simple cyanides of 55, 61, and 71 percent in the final effluent. These percentages would represent the cyanide remaining after treatment, where presumably some fraction of the simple cyanides in the wastewater would have been removed.

As described in Chapter 1, simple cyanide reacts with a number of metals to form complex metallocyanide anions. Copper, nickel, iron and zinc are common refinery wastewater metals that will react with simple cyanide. These metals are present in crude oil, the refinery process water used for steam generation and cooling, some chemical additives and catalysts, and in the materials of construction of the refinery equipment. Thus, it can be assumed that some fraction of the total cyanide that is present in the sour water from a thermal process will be present as complexed cyanide. The relative proportions of the total cyanide that are complex and simple cyanide will depend on the quantity and type of metal ions that are present in the wastewater and will be site-specific. However, the iron released by the corrosion of carbon steel equipment that is exposed to the sour gases containing cyanide will usually be the source of the majority of the complexed cyanide in refinery wastewater.

Corrosion of carbon steel equipment that is exposed to gases and water containing hydrogen sulfide and hydrogen cyanide has received considerable attention by the refining industry through the years. This corrosion of iron and the subsequent reaction with simple cyanide forms ferrocyanide anion $[\text{Fe}(\text{CN})_6]^{4-}$ and ferricyanide anion $[\text{Fe}(\text{CN})_6]^{3-}$. Both of these iron-cyanide complexes are very stable to pH and chemical changes (Kunz, R.G., Casey, J.P. and Huff, J.E., 1978).

A common practice to control corrosion in thermal process equipment is the addition of sodium and ammonium polysulfide, which reacts with the simple cyanide generated in the process to form thiocyanate (Kunz, R.G., Casey, J.P. and Huff, J.E., 1978). Studies conducted in the 1970's demonstrated that when polysulfide was added to the fluid catalytic cracking unit to convert simple cyanide to thiocyanate, the total cyanide concentration in the sour water sent to the stripper was substantially reduced. This is because a substantial portion of the total cyanide generated in

the catalytic cracking unit was free or simple cyanide. The sour water stripper effluent total cyanide concentration remained essentially unchanged with polysulfide addition to the influent because the total cyanide in its influent was all complexed cyanide, that will not react with the polysulfides.

The injection of polysulfides into catalytic cracking units has been successfully used by refineries to convert simple cyanides to thiocyanates. Because EPA's water quality criterion is for free cyanide, this chemical conversion allows refineries to comply with their water quality-based effluent limits for cyanide. Even when a state uses total cyanide as its water quality criterion, the conversion of cyanide to thiocyanates will eliminate total cyanide in the effluent if the conversion is complete.

Summary

The process sources of cyanide in petroleum refineries are limited. The catalytic cracking and thermal cracking processes at a refinery will generate virtually all of the cyanide found in refinery wastewaters. The sour water generated by the thermal processes will contain the cyanide. This is because the thermal processes operate at reducing conditions (high temperatures, no oxygen) that promote the formation of reduced nitrogen and sulfur compounds, i.e., cyanide and sulfides. Although both sulfides and cyanides are formed under these reducing conditions, there is no consistent quantitative correlation between these two chemical species because their concentrations in sour water are a function of the nitrogen and sulfur content of the process feed, which is a function of the feedstock source and is highly variable.

The nitrogen content of the crude petroleum processed by a refinery is a determinant of the amount of cyanide that potentially may be generated, but no useful quantitative correlation between crude petroleum nitrogen content and the mass of cyanide generated was found by the literature review conducted for this study. Based on the chemistry of nitrogen compounds, the cyanide precursors in the refinery thermal processes are organic nitrogen chemicals and are not formed from inorganic nitrogen salts.⁶

The cyanide that is present in refinery wastewater is a mixture of stable complexed cyanide, primarily iron-cyanide complexes, and simple cyanide. Because simple cyanide is treatable, i.e., removed by steam stripping and by biodegradation and complexed cyanides

⁶ As described in Chapters 4 and 5, cyanide can be formed from inorganic organic chemicals by the chemical reactions used for some of the analytical methods. These chemical reactions do not occur in petroleum refining processes.

are typically not removed very effectively by refinery wastewater treatment processes, the total cyanide concentration in final effluents may contain a relatively high proportion of complexed cyanide. Thus, refineries should work with their regulatory agency to assure that they can use an analytical method for simple cyanide to demonstrate compliance with an NPDES permit limit based on “free” cyanide. Based on the authors’ experience with cyanide WQBELs in Texas NPDES and TPDES permits for petroleum refineries, the weak acid dissociable (WAD) method for simple cyanide will generally demonstrate compliance with free cyanide WQBELs because the simple cyanide concentrations in biologically treated refinery effluents are generally quite low.

If a state, tribe, or EPA Region insists that a water quality-based effluent limit must be based on total cyanide rather than free cyanide, then the permittee should insist that the total cyanide limit be based on a quantitative site-specific correlation between free and total cyanide in its wastewater. The permittee should not have to settle for the conservatism of measuring total CN to comply with a free CN permit limit. Use of a site-specific free-total cyanide correlation is particularly important if the permittee is required to use the total CN analysis for compliance determinations.

Cyanides are found in wastewaters from a number of industrial categories in addition to petroleum refining. In fact, the cyanide concentrations found in petroleum refinery effluent are generally lower than the concentrations found in wastewaters from other manufacturing industries.

Since 1990, publicly owned treatment works (POTWs) have also been found to have low, but measurable, cyanide concentrations in their discharges. These low concentrations were historically considered unimportant by the regulators and the POTW community, but with the implementation of the water quality criteria for cyanide in NPDES permits some POTWs have found that they cannot consistently comply with their cyanide WQBELs.

The following sections provide an overview of industrial and POTW cyanide discharges to surface waters. These data place in perspective the petroleum refining industry discharges of cyanide described in Chapter 3.

Industrial Discharges

There are a number of industrial categories for which EPA has developed technology-based effluent limitations guidelines and pretreatment standards for cyanide, pursuant to the requirements of Sections 301, 304, 306 and 307 of the Clean Water Act. These industrial categories were deemed to have processes that generated sufficient cyanides that national technology-based guidelines and pretreatment standards were required. Table 2 lists the industrial categories that include effluent limitations guidelines or pretreatment standards for cyanide in one or more subcategories.

This summary indicates that cyanide is discharged to surface waters by a number of major industrial categories in quantities that are sufficiently large so as to merit the promulgation of national effluent limitations guidelines and pretreatment standards. To obtain a better estimate of the relative quantities of cyanides discharged by industry, the 2001 toxics release inventory (TRI) database was queried for surface water discharges. Table 3 presents the results of that analysis.

Table 2
Industrial Categories with EPA Technology-based Limits
For Cyanide¹

Industry	Regulation	Subcategory	Total Cyanide Limits	Cyanide Amenable to Chlorination Limits
Electroplating	40 CFR 413	Electroless plating	No	Yes
Organic Chemicals	40 CFR 414	Appendix A (CN-bearing)	Yes ²	No
Inorganic Chemicals	40 CFR 415	Hydrogen cyanide	No	Yes
Iron and Steel	40 CFR 420	Coke, sintering, ironmaking	Yes	No
Metal Finishing	40 CFR 433	All	Yes	No
Pharmaceuticals	40 CFR 439	CN-bearing streams	Yes	No
Pesticides	40 CFR 455	CN-bearing streams	Yes	No
Coil coating	40 CFR 465	Steel, galvanized, and aluminum basis	Yes	No

¹Effluent limitations guidelines and pretreatment standards have been promulgated for most major industrial categories.

²The rule allows plants to demonstrate that the cyanide in their effluent is complexed cyanide and, in such cases, to establish alternative limits for amenable cyanide.

Table 3
2001 TRI Releases of Cyanide to Surface Waters¹

Industry Category	Releases to Surface Water (pounds)	Percent of Total Releases
Chemicals	4,932	4.79
Petroleum	265	0.26
Primary Metals	94,649	91.98
Fabricated Metals	150	0.15
Electrical Equipment	15	0.01
Miscellaneous	254	0.25
Multiple SIC Codes (20-39)	434	0.42
No Reported Code	250	0.25
Metal Mining	1,949	1.89
Chemical Wholesalers	5	0.00
Total	102,903	100.00

¹Reported as cyanide compounds and hydrogen cyanide

As shown by the data in Table 3, the reported releases of cyanide by petroleum refineries to surface waters were 0.26% of the industry total reported in the 2001 TRI. Because the TRI does not require reporting by all industrial categories and has size cutoffs for reporting, refineries constitute an even smaller fraction of the total annual cyanide discharges to U.S. surface waters than is shown in Table 3.

POTWs have not historically been considered to be significant point sources of cyanide. The industrial categories that are potentially significant indirect dischargers of cyanide all have national pretreatment standards that they must comply with. POTWs are also required to set local pretreatment limits for pollutants, such as cyanide, if they determine that such pollutants will pass through or interfere with the treatment system.

Although POTW operators and regulatory agencies did not consider POTWs to be major point source dischargers of cyanides, EPA performed comprehensive sampling studies at POTWs in 1980 and 1981 which showed that many POTWs did discharge cyanide in measurable amounts (Burns and Roe Industrial Services Corp., 1982). The cyanide data from EPA's "40 POTW" sampling study are summarized in Table 4.

Table 4
POTW Cyanide Effluent Discharges¹

POTW Identifications	Percent of Samples where Detected	Minimum CN (µg/L)	Maximum CN (µg/L)	Median Percent Removal ²
POTWs 1-40	97	2	2,140	59
POTWs 51-60	56	10	400	59

¹All POTWs had a minimum of secondary (biological) treatment in place. There were no POTWs numbered 41-50 in this study.

²Median percent removal was calculated with data from all POTWs. Note that the low median percent removal was primarily due to low influent concentrations and high cyanide analytical detection limits.

These data indicate that POTWs have always been potentially significant point sources of cyanides even though they were generally not considered to be such until recently (i.e, after states begin implementing WQBELs more rigorously).

When states began implementing more rigorously derived WQBELs in NPDES permits issued in the 1990's, some POTWs found that they were given permit limits for cyanide that they could not comply with 100% of the time. Depending upon the state issuing the permit, these limits were based on either on free cyanide (typically expressed as either amenable cyanide or WAD cyanide) or total cyanide. Compliance problems were generally most acute for POTWs that discharged to surface water bodies where allowable mixing zone dilutions provided for by state regulations were $\leq 10\%$ effluent.

Because of these compliance difficulties, several government agencies responsible for municipal sewage treatment joined with

several manufacturers and trade associations to fund research to study the formation of cyanide compounds in treatment systems and to evaluate the capabilities and limitations of the analytical methods for all forms of cyanide. This research was conducted through a grant (98-HHE-5) from the Water Environment Research Foundation (WERF)(Alexandria, Virginia), which provided funding in addition to that provided by the industrial and municipal contributors. The grant was awarded in 1998 to a consortium consisting of university researchers and consulting firms. In addition, several manufacturers and municipalities participated directly in the WERF project by analyzing wastewaters with specified analytical methods.

One of the studies performed under the grant investigated the potential for the formation of total cyanide and free cyanide in POTW pretreatment processes (Zheng, A., Dzombak, D.A., Luthy, R.G., 2001). These studies were designed to address observations that some POTWs that had no measurable free or total cyanide in their influents had detectable concentrations of both species of cyanide in their effluents.⁷

The research found that free and total cyanide could be generated by POTW treatment processes by the following mechanisms:

- Incomplete oxidation of thiocyanate with chlorine when insufficient chlorine is applied to completely oxidize thiocyanate.
- Ultraviolet irradiation of thiocyanate.
- Chloramination that occurs when hypochlorite reacts with ammonia in the presence of certain precursor organic compounds (e.g., benzene, L-serine), which forms cyanogen chloride and traces of free and total cyanide when the wastewater is dechlorinated. This reaction can occur in the samples collected for analysis, because the analytical method requires dechlorination of the sample.
- Nitrosation of organic compounds when nitrites are present in the wastewater. It was also found that if the sulfamic acid required by the analytical method to prevent cyanide formation is added after extended sample holding times, the acid may actually convert some organic compounds in the sample to cyanides.

This research demonstrates that cyanides can be formed in POTW treatment units under certain conditions. Chlorination with either free chlorine or hypochlorite and UV irradiation are the

⁷ Other WERF project studies dealt with analytical methods and are discussed in Chapter 5.

disinfection processes used at virtually all POTWs. Nitrites are commonly present at low concentrations in biological treatment unit effluents that are operated to nitrify ammonia. When the nitrification process is upset, nitrites can be present in the effluent in the mg/L concentration range, thus increasing the potential for cyanide formation.

The findings of this study are also relevant to the potential formation of cyanide in industrial wastewater treatment plants. While chlorination and UV irradiation are not commonly required for effluent disinfection at industrial plants, chlorine and hypochlorite are used to control bulking in activated sludge units and could generate cyanides. Industrial biological treatment units that nitrify ammonia also will generate nitrites and the observations in this study that nitrites can form cyanides when they react with residual organic compounds in the wastewater may also be relevant for some industrial wastes.

As described in Chapter 1, cyanides can occur in aqueous solution associated with a number of different cations and the toxicity of a cyanide compound to aquatic life is dependent upon the associated cation, which determines the stability of the compound. The analytical methods for cyanide and related compounds include procedures for total CN, simple CN compounds, free CN, thiocyanate, and cyanogen chloride. The following descriptions of cyanide methods are focused on procedures that can analyze for cyanide forms in the 0.001 mg/L to 0.020 mg/L (1 to 20 µg/L) range because this is the range of concern for water quality standards compliance and some WQBELs. However, other methods that can be used for higher concentrations of cyanides and related compounds are identified because they may be useful for source identification studies.

Table 5 lists the available analytical methods for different forms of CN and indicates their approval status at 40 CFR 136. Methods that are not listed in 40 CFR 136, but that have been approved by EPA for one or more permittees as an alternative method, are also shown. Because 40 CFR 136.4 provides for approval of alternative analytical methods for compliance testing, methods shown in Table 5 that are not currently approved can be approved on a site-specific basis (or for a category of discharges) if the necessary data are supplied to EPA for approval.

EPA has acknowledged that cyanide is a “method-defined” analyte (64 Federal Register 73414, December 30, 1999). A method-defined analyte measures the concentration of a chemical and/or group of chemicals in an unknown sample that have certain properties that are measured by the analytical method. A method-defined analyte is not a unique chemical or chemical compound.

Analytical methods for related cyanide-containing compounds are summarized in Table 6.

Table 5
Analytical Methods for Cyanide Forms

Method Description	Reference ¹	Cyanide Form Measured ²		Approved at 40 CFR 136
		Total Cyanide	Simple Cyanides	
Total CN after distillation [CN(T)] — spectrophotometric or titrimetric detection	EPA 335.2; SM 4500-CN ⁻ C, D, E; D 2036-98(A)	√		√
Total CN after distillation — ion selective electrode detection	SM 4500-CN ⁻ F	√		√
Automated CN(T) by UV digestion, distillation, spectrophotometric detection	EPA, 335.3	√		√
Automated CN(T) by UV digestion, thin film distillation, spectrophotometric detection	D 4374-93	√		
Available CN [CN(A)] — as cyanide amenable to chlorination, spectrophotometric or titrimetric detection	EPA 335.1; SM 4500-CN ⁻ G; D 2036-98(B)		√	√
Weak Acid Dissociable CN [CN(W)] — spectrophotometric, titrimetric, or ion selective electrode detection	SM 4500-CN ⁻ I		√	√ ³
CN(A) by ligand exchange, flow injection, amperometric detection	OIA-1677; D 6888-03		√	√
Free CN by microdiffusion, spectrophotometric detection	D 4282-02		√	
CN(T), CN(A), CN(W) by distillation, ion chromatography, amperometric detection	Modified EPA 335.1 or SM 4500-CN ⁻ G		√	√ ³

¹EPA — *Methods for Chemical Analysis of Water and Waste*, EPA 600/4-79-020, EMSL, Cincinnati, OH, 1979, revised 1983; SM — *Standard Methods for the Analysis of Water and Wastewater*, 18th ed., APHA, Washington, D.C., 1992; D — ASTM Standards; OIA — OI Analytical (ALPKEM), College Station, TX

²EPA refers to simple cyanide as available cyanide; the ASTM method refers to “free” cyanide; both measure simple cyanides as they are described in Chapter 1.

³Approved by EPA as a site-specific alternative analytical method for one or more NPDES permittees.

Table 6
Methods for Cyanide-Related Analytes

Method Description	Reference ¹	Compound Measured
Cyanogen chloride by spectrophotometric detection	SM 4500-CN ⁻ F	CNCl
Cyanates by ion-selective electrode	SM 4500-CN ⁻ L	OCN ⁻
Thiocyanates by spectrophotometric detection	SM 4500-CN ⁻ M; D 4374-00	SCN ⁻
Metal cyanides by ion chromatography, UV detection	Dionex Corp.	Fe, Ni, Cu, Co, Pt, Pd, Ag, Au cyanides

Description of Methods for Cyanide Analysis

The following brief summaries of the analytical methods for cyanides and related compounds are intended to provide the reader with an understanding of the scope and limitations of the most widely used methods. Subsequent sections of this report describe interferences and the performance of the methods. The cited references for each analytical method must be read to obtain the details of the methods, their appropriate application, and their limitations.

The analytical methods for total and simple CN all use the same types of detection methods. The differences in the methods are primarily in the preparation of the solution that is analyzed for the CN⁻ group, after it has been separated from interfering compounds. The detection methods used are spectrophotometric (colorimetric), amperometric, ion selective electrode, and titrametric. These detection methods are described immediately following the summaries of the analytical methods.

Total CN

Distillation

The EPA-approved distillation methods for CN(T) (EPA 335.2, SM 4500-CN⁻C; D 2036-98(A)) liberate HCN gas from an aqueous sample that is acidified with sulfuric acid and boiled to distill off the gas. The boiling flask is purged with air and the HCN gas is collected in a sodium hydroxide scrubbing solution. The cyanide concentration in the scrubbing solution is determined by titrimetric, colorimetric, or potentiometric (ion selective electrode, amperometric) procedures (APHA, 1999). Automated versions of the distillation methods are available (D 4374-00; EPA 335.3).

The strong acid distillation methods are designed to release CN from the most stable metalocyanide compounds, such as the ferricyanides. However, cobalticyanide is not recovered completely because CN catalytically decomposes in the presence of cobalt in strong acids at high temperatures. The method also may not completely recover cyanide complexes of noble metals (e.g., gold, platinum). These limitations on the quantitation of certain metalocyanide compounds are not likely to be important for petroleum industry wastewaters.

Ultraviolet Digestion

Ultraviolet (UV) digestion of metalocyanide complexes in an aqueous sample that is mixed with heated phosphoric acid is an alternative to the sulfuric acid digestion process (EPA Method 335.3; SM 4500-CN⁻O, proposed; ASTM D 4374-00). The HCN in the digested “donor” stream is collected by passing the donor stream across a gas permeation membrane and collecting the HCN in a parallel “acceptor” stream of dilute sodium hydroxide. The sodium hydroxide acceptor stream is equivalent to the sodium hydroxide scrubbing solution in the distillation method.

Alternatively, the digested stream is distilled as described above. Method 335.3 (automated, UV digestion, distillation, colorimetric detection) is approved for NPDES permit compliance analyses.

The low power UV digestion method is not approved at 40 CFR 136 for NPDES compliance monitoring. EPA has evaluated the low power UV method for total CN analysis but has withheld approval pending resolution of concerns that it does not digest metalocyanides as completely as the distillation methods.

However, approval of the low power UV digestion method as site-specific alternate analytical methods under 40 CFR 136 should be possible if the required method performance demonstration can be achieved.

Distillation and Ion Chromatography

Sulfide is a major interference in the spectrophotometric and amperometric determinations of cyanide. Because sulfide distills overhead to the sodium hydroxide scrubber solution and will react with the color reagents required for spectrophotometric analysis, and will give a signal that cannot be distinguished from cyanide in the amperometric detection methods, the interference must be eliminated before a sample can be successfully analyzed for cyanide. The cyanide methods specify the addition of lead acetate and/or lead carbonate to the sample during acid digestion to remove the sulfide interference.⁸ However, many users of the standard methods have found that this interference correction is inadequate for their wastewaters, especially at low cyanide concentrations.

The use of ion chromatography and amperometric detection to unambiguously separate sulfide and cyanide collected in the sodium hydroxide scrubber solution has been shown to eliminate this interference (Matz, S.G., 1996). The ion chromatograph separates the cyanide peak from the peaks of sulfides and thiocyanates so that they don’t register as interferences on the

⁸ The lead carbonate or lead acetate is added to the digestion vessel in the laboratory. The presence of sulfide in the sample prior to digestion and distillation (i.e., the preserved sample) does not interfere with the test.

amperometric detector. The ion chromatographic separation step has also been proven to reduce other, unknown interferences, that are present in the effluent from a regional wastewater treatment plant that treats a mixture of refinery, chemical plant, and pulp and paper mill wastewaters. This method has been approved by EPA as an alternative analytical method for total cyanide — CN(T), available cyanide — CN(A), and weak acid dissociable cyanide — CN(W) analyses on a site-specific basis at this regional treatment plant and for certain other industrial plants.

Simple CN

Available Cyanide

The historically most widely used method for simple cyanide in aqueous matrices is referred to by EPA as available cyanide [CN(A)] and is commonly measured as cyanide amenable to chlorination (also referred to as CATC in some references). It is an approved method at 40 CFR 136 (EPA Method 335.1; SM 4500-CN⁻G; D 2036-98(B)), despite the fact that it is subject to serious matrix interferences in a number of wastewaters (63 Federal Register 36810, July 7, 1998).

This method involves distillation of two samples: (1) the original sample; and (2) an aliquot of the sample that has been chlorinated to destroy all “amenable” cyanide that is present. The two samples are distilled and analyzed as described above for the total CN method. The difference between the concentration in the two samples is reported as CN(A).

The CN(A) method is subject to numerous matrix interferences. The most common interference from a petroleum industry standpoint is that some unknown compounds in complex effluents, including petroleum refinery wastewaters, react with chlorine and generate compounds that measure positively as CN in the test (APHA, 1999). When this interference occurs, negative values of CN(A) are the result⁹ and the method is not usable and the negative values must be considered invalid.¹⁰ The CN(A) analytical method (SM 4500-CN⁻G)¹¹ instructs the analyst to use the weak acid dissociable method to report available cyanide as CN(W) when a CATC sample analysis results in negative CN(A) concentrations.

⁹ Because CN(A) is calculated as the difference in the measured CN(T) values before and after chlorination of the sample.

¹⁰ Users of this method must be careful to assure that labs report CN(A) results correctly. The authors experienced a situation where a commercial laboratory was reporting negative CN(A) values as zero (0) and the NPDES permit holder was reporting these zero values in discharge monitoring reports as “not detected” values.

¹¹ EPA Method 335.1 does not acknowledge possible negative results for the CN(A) analysis and thus gives no instructions on how to obtain valid results for such samples.

Weak Acid Dissociable Cyanide

CN(W) (also known as WAD CN, SM 4500-CN⁻) uses a weakly acidified (acetic acid to pH 4.5-6.0) digestion solution and distillation to release simple cyanides from aqueous samples. A zinc salt in the acetate buffer used to adjust solution pH assures that iron cyanides are precipitated and not measured by the method. The sodium hydroxide scrubber solution that collects the HCN distilled from the sample is analyzed as described earlier in the methods for CN(T).

The CN(W) method is not listed in 40 CFR 136. However, many permitting authorities (both state and EPA) allow it to be used for demonstrating compliance with a free cyanide permit limit. Because the CN(A) method directs analysts to use the CN(W) method for determining available cyanide when interferences occur, permit authorities generally consider the two methods to be equivalent.¹² Also, EPA acknowledges in the final rulemaking for Method OIA-1677 that CN(A) and CN(W) are equivalent (64 Federal Register 73414, December 30, 1999). Some states (see Chapter 2) require that the CN(W) method be used to demonstrate compliance with a water quality-based effluent limit. The permittee should assure that its permit specifically identifies the CN(W) method for compliance monitoring unless the state water quality standards and implementation procedures unambiguously allow or require the CN(W) method for monitoring and compliance.

Free Cyanide by Microdiffusion

This ASTM method (D 4282-02) measures the same simple cyanide compounds as the CN(A) and CN(W) methods although the method uses the term “free” cyanide to describe the result. The analysis is performed by separating the CN(F) from the water sample in a cylindrical microdiffusion cell with two annular compartments. The sample is placed in the outer compartment, the pH is adjusted to 6 with a buffer, and dissolved cadmium is added to precipitate any hexacyanoferrate that is in the sample. The inner compartment is filled with a dilute sodium hydroxide solution. The cell is then sealed and held at room temperature in the dark for 4 hours. HCN released from the sample diffuses through the cell headspace into the sodium hydroxide solution. The sodium hydroxide solution is then analyzed colorimetrically using the

¹² These states take the position that because the CN(A) test is approved at 40 CFR 136, and the CN(A) test directs the user to the CN(W) test when interferences occur, that the CN(W) test is *de facto* an approved method. In addition, states have latitude in their water quality standards to specify the method of measurement used for a water quality criterion. For example, Washington specifically identifies the CN(W) test for determining compliance with their cyanide criteria.

same method as that used in the CN(T), CN(A), and CN(W) procedures.

Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry

This method for CN(A) is commercialized and has been approved by EPA at 40 CFR 136 (Method OIA-1677; D 6888-03). Prior to analysis, ligand exchange reagents are added to the aqueous sample to release the cyanide anion from metallocyanide compounds.¹³ The analysis is performed in a proprietary cyanide analyzer.

The treated samples (after ligand exchange) are placed in an autosampler and injected into the flow injection manifold of the analyzer and mixed with a hydrogen chloride carrier/reagent. The cyanide ions in the sample are converted to HCN that diffuses through a gas diffusion membrane into a dilute sodium hydroxide acceptor solution. The cyanide ion in the acceptor solution is then measured amperometrically.

Detection Methods

Spectrophotometric (Colorimetric) Detection

The alkaline absorption solution (distillate, permeate) is treated with chloramine-T at pH < 8 to convert CN⁻ to cyanogen chloride (CNCl). A pyridine-barbituric acid reagent is then added to the solution and reacts with the CNCl to form a red-blue color that is measured with a spectrophotometer (maximum color absorbance between 575 and 582 nm). SM 4500-CNE describes this method in detail.

Standard Methods states that the spectrophotometric method is suitable for measuring CN at concentrations as low as 1 µg/L. However, as discussed later in this chapter, detection limits below 1 µg/L have been achieved with this method in the absence of interferences.¹⁴

¹³ The ligand exchange reagents specified by the manufacturer are proprietary. However, the method allows substitution of ligand exchange reagents. Examples of substitute reagents are given by Zhang, A., et.al., 2003.

¹⁴ The detection limits cited in this section are those that have been achieved on specific effluent matrices in the absence of interferences, by experienced laboratories. These detection limits may not be achievable for complex effluents.

Potentiometric Detection

This category of detection methods includes both ion selective electrodes (see SM 4500-CN⁻F) and amperometric detectors such as that used in Method OIA-1677 and the ion chromatography analytical system.

The ion selective electrode method uses a cyanide-specific electrode and a reference electrode that are calibrated with a standard KCN solution. *Standard Methods* states that this method is suitable for CN⁻ concentrations as low as 50 µg/L. However, site-specific studies have shown that a method detection limit (MDL) of 5 µg/L can be achieved in an effluent matrix using this detection method.

The amperometric detection method used in Method OIA-1677 uses a silver electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter electrode for quantifying CN⁻ concentrations in the absorbent solution. The Dionex Corp. ion chromatograph system has a pulsed-electrochemical detector (Matz, S.G., 1996). Method OIA-1677 indicates that it has an MDL of 0.5 µg/L in reagent water. The amperometric detector used in the ion chromatography system has been demonstrated to achieve an MDL of < 1 µg/L (Matz, S.G., 1996).

Titrametric Detection

The CN⁻ in the alkaline absorption solution is titrated with standard silver nitrate to form soluble silver cyanide complex. When all CN⁻ in the solution is complexed, a small excess of silver is detected by the indicator reagent p-dimethylaminobenzalrhodamine (SM 4500-CN⁻D). This detection method is only suitable for wastewaters containing greater than 1 mg/L CN⁻. Therefore, it is not suitable for evaluating effluents for compliance with WQBELs but may be useful when performing source evaluation studies.

Related Compounds

Thiocyanates

Wastewater containing SCN⁻ is chlorinated to form cyanogen chloride (CNCl). The wastewater is acidified to pH 2 with concentrated nitric acid and ferric nitrate is added to form an intense red color for colorimetric determination (SM 4500-CN⁻M). An automated method is available (D 4374-00).

The wastewater sample must be pretreated to remove highly colored and/or interfering organic compounds. Pretreatment consists of passing the acidified wastewater through a prepared macroreticular adsorption resin. A solvent extraction technique

may be substituted as an alternative method for removing interfering compounds.

If the sample contains CN(A) and is to be preserved at high pH for cyanide analysis, sulfide must be removed by the addition of lead salts (lead acetate/lead carbonate) before adding the alkali preservative. The precipitated solids must be filtered from the treated sample before the pH is elevated.

Standard Methods indicates that this method can measure SCN^- in the concentration range from 0.1 mg/L to 1.0 mg/L in wastewater or natural waters.

Cyanates

Cyanate (OCN^-) hydrolyzes to ammonium ion when heated at low pH. The liberated ammonium ion is quantified with an ion-selective electrode. The ammonium ion present in the sample before the hydrolysis of OCN^- is also measured and the difference in the ammonium ion concentrations is used to determine the concentration of OCN^- present in the sample (SM 4500-CN⁻L).

Cyanate is unstable at neutral or low pH; samples must be preserved when collected by adding sodium hydroxide to $\text{pH} > 12$. Chlorine residual must be removed by adding sodium thiosulfate to the sample.

Standard Methods does not give any information on the detection limit achievable by this method.

Cyanogen Chloride

Cyanogen chloride (CNCl) is measured colorimetrically as described in the summary of analytical detection methods in *Standard Methods* (SM 4500-CN⁻J). Because CNCl hydrolyzes to OCN^- at high pH, wastewater samples for this analyte must be preserved separately from samples for CN(T) and simple cyanides. Sodium thiosulfate must be added to samples if residual chlorine is present.

Standard Methods does not give any information on the detection limit achievable by this method.

Metal Cyanides

Cyanide forms multi-ligand complexes with many metal ions, as described in the introduction. These anionic complexes can be separated by ion chromatography and measured with a suitable detection method (Zheng, A., et.al., 2003). A method capable of measuring metal cyanide complexes containing iron, nickel, copper, cobalt, platinum, palladium, silver, and gold has been

developed. The method uses anion exchange columns and detection by UV absorbance.

Method detection limits in the range from 1 µg/L to 10 µg/L have been reported for this method (Zheng, A., et.al., 2003).

Method Performance

The performance of the cyanide methods is characterized in terms of achievable detection and quantitation limits and recovery and precision. Because the emphasis of this report is on the lowest concentrations of cyanide compounds present in wastewater and natural water, the data presented focus on measurements in the 1-20 µg/L range.

Detection and Quantitation Limits

The references on the analytical methods for cyanides typically present the method detection limit (MDL) that has been promulgated by EPA at 40 CFR 136, Appendix B. Although there is controversy in the regulated community over whether or not the EPA MDL is an adequate representation of the true detection level of an analytical method, it is a convenient means of comparison for analytes, matrices, and methods. Because the MDL is matrix-specific in most cases, the published MDLs shown in this report will not be achievable in all wastewater matrices. This is particularly true for complex matrices such as industrial and municipal wastewaters prior to secondary (biological) treatment.

Table 7 presents the MDLs shown in the references available for the cyanide methods discussed in this report. The MDLs shown are the lowest concentration values reported for each method. Methods with higher achievable MDLs (e.g., the titration method of detection) are not shown because they are not generally relevant to water quality criteria and WQBELs in NPDES permits. Also, the MDLs shown in this table represent analysis of relatively “clean” samples such as surface waters and effluents that have received at least biological treatment. These MDLs would not be generally achievable in untreated wastewaters and similarly complex matrices.

The paper by Zheng, A., et.al. (2003) is the best single reference currently available on detection limits, precision, and recovery for the principal cyanide species of interest to the petroleum industry. This paper describes method performance studies conducted as part of the WERF Grant No. 98-HHE-5 project and involved evaluation of seven analytical methods by six laboratories, each of

which analyzed five “contaminated water” samples¹⁵ and one reagent water sample.

Table 7
Method Detection Limits for Cyanides

Analyte	Method	Matrix	MDL (µg/L)	Reference
CN(T)	Distillation, spectrophotometry	Reagent water	5	SM 4500-CN ⁻ C, E; ¹
	Low power UV digestion, distillation, spectrophotometry	Reagent water	1	Zheng, A., et.al., 2003
		5 CW samples ²	1	
	Distillation, ion-selective electrode	Reagent water	50	SM 4500-CN ⁻ C, F
		Chemical plant effluent	10	Unpublished site-specific study
	UV digestion, thin film distillation, spectrophotometry	Reagent water	5	Zheng, A., et.al., 2003
		5 effluents	5	
	Distillation, ion chromatography, amperometry	Reagent water	1	Matz, S.G., 1996
CN(A)	Chlorination, distillation, spectrophotometry ³	Reagent water	5	SM 4500-CN ⁻ C, E;
	Ligand exchange, flow injection, amperometric analysis	Reagent water	0.5	OIA-1677
		Reagent water	0.5	Zheng, A., et.al., 2003
		5 effluents	5	
CN(W)	Distillation, spectrophotometry	Reagent water	5	SM 4500-CN ⁻ I, E
		Reagent water	1	Zheng, A., et.al., 2003
		5 effluents	2	
	Automated, thin-film distillation, spectrophotometry	Reagent water	1	
		5 effluents	1	
CN(F)	Microdiffusion, spectrophotometry	Reagent water	1	Zheng, A., et.al., 2003
		5 effluents	2	
Metal CN	Metal cyanides by ion chromatography, UV detection	Reagent water	2	Zheng, A., et.al., 2003
		5 effluents	10	
SCN ⁻	Spectrophotometry	Reagent water	100	SM 4500-CN ⁻ M

¹ Values reported in *Standard Methods* are not MDLs developed pursuant to 40 CFR 136, Appendix B. They are reported as the lower end of the effective method range.

² CW — “contaminated water” samples. See footnote 7 for complete description.

³ MDLs shown for cyanide amenable to chlorination should be considered with care. They are the detection limits in the wastewater but because this method involves the subtraction of two very small numbers, the MDLs are probably overstated.

The technical references reviewed for this paper do not present quantitation limits.¹⁶ EPA uses the term “minimum level” (ML) to describe a concentration level that it considers to be equivalent to a

¹⁵ The “contaminated water” samples were: (1) groundwater from a manufactured gas plant site; (2) unchlorinated POTW secondary effluent; (3) chlorinated effluent from the same POTW as in 2; (4) POTW primary clarifier effluent; and (5) groundwater from an aluminum smelting plant site.

¹⁶ As used in this report, a quantitation limit is the concentration level where a measured concentration can be reported within a defined precision of the “true” concentration in the sample (e.g., ± 40%).

quantitation level. States and other EPA programs may use other terminology for quantitation levels including: minimum quantitation level (MQL), practical quantitation level (PQL), and minimum analytical level (MAL).

EPA considers the ML to be equivalent to the MDL multiplied by a factor of 3.18 (result rounded to the next highest 2, 5, or 10 value in the concentration range). Therefore, the EPA ML for the cyanide methods shown in Table 7 can be approximated by multiplying the MDL values shown in the table by 3.18 and rounding them following EPA practice. Thus, for MDLs shown in Table 7 as 5 µg/L, the ML would be 20 µg/L ($5 \mu\text{g/L} \times 3.18 = 15.9 \mu\text{g/L}$ rounded up to 20 µg/L).

Table 8 presents examples of the quantitation levels for cyanide that selected states and EPA have used in their NPDES permitting and water quality standards programs.

Table 8
State and EPA Quantitation Levels for Cyanide

Cyanide Form	Quantitation Level (µg/L)	State/EPA Region/EPA Method
CN(F)	5	EPA Method 335.3 ¹
CN(T), CN(A)	20	EPA Methods 335.1 ¹ , 335.2 ¹
CN(A)	2	Method OIA-1677
CN(T), CN(A)	10	EPA Region 6
CN(not specified)	5	California
CN(F)	20	Texas
CN(T), CN(A)	10	Louisiana
CN(T), CN(A)	10	Oklahoma
CN(not specified)	40	New Jersey
CN(T)	1	Pennsylvania ²
CN(F)	Not specified	
CN(W)	5	Washington ³

¹These are not quantitation levels in the strict use of the term. They are the lower end of the operating range of the method.

²Pennsylvania uses an MDL, not a quantitation limit, for compliance. They allow use of the CN(W) tests for demonstrating compliance with their CN(F) criterion but give no required detection limit in their regulations.

³Washington uses an MDL for NPDES compliance.

The MDL method at Appendix B of 40 CFR 136 recommends developing matrix-specific MDLs for complex effluents. Most states will also accept matrix-specific quantitation limits if an NPDES permittee conducts the analyses required to demonstrate the achievable level. The authors have worked with two plants that have developed matrix-specific quantitation limits for CN(A) that are 40 µg/L and 60 µg/L, respectively, that were approved by the state. Both of these effluents contained many interfering unknown

compounds and the matrix-specific quantitation levels were granted after demonstrations that the published methods for removing interferences were ineffective.

Precision and Recovery

The best reference for the precision and recovery of simple cyanide in aqueous matrices is the multi-laboratory study performed as part of the WERF Grant No. 98-HHE-5 project (Zheng, A., et.al., 2003). Samples of reagent water and five contaminated water samples were spiked with three forms of cyanide: (1) sodium cyanide (NaCN), (2) potassium-nickel cyanide ($K_2Ni(CN)_4$), and (3) potassium ferricyanide ($K_2Fe(CN)_6$) for the precision and recovery analyses of seven analytical methods for cyanide species. The results of the low level (5 µg/L) spike analyses for the two simple cyanide compounds evaluated (sodium cyanide, potassium-nickel cyanide) are summarized in Table 9.

Table 9
Precision and Recovery of a 5 µg/L Spike of Simple Cyanide
in Various Aqueous Matrices
(Zheng, A., et.al., 2003)

Analyte	Method	Matrix	Relative Standard Deviation (%)	Recovery (%)	Bias (µg/L) ²	
					NaCN	$K_2Ni(CN)_6$
CN(T)	UV digestion, thin film distillation, spectrophotometry	Reagent water	1.69-4.20	68.57-128.6	-1.57	1.43
		5 CW samples ³	2.22-10.4	66.57-157.5 ³	-0.13/-7.01	-41.59/2.88
	Low power UV digestion, distillation, spectrophotometry	Reagent water	8.24-23.0	70.71-90.49	-0.48	-1.46
		5 effluents	1.92-11.3	17.56-97.42	-0.2/0.78	-0.08/-3.59
CN(A)	Ligand exchange, flow injection, amperometric analysis	Reagent water	6.61-6.65	102.7-108.0	0.41	0.14
		5 effluents ⁴	4.43-19.6	102.7-138.6	1.51/1.95	0.4/1.64
CN(W)	Distillation, spectrophotometry	Reagent water	3.92-4.44	100.4-103.7	0.18	0.02
		5 effluents	1.98-14.2	71.06-147.0	-1.02/0.91	-1.81/2.59
	Automated, thin-film distillation, spectrophotometry	Reagent water	1.99-2.64	100.6-113.7	0.03	0.69
		5 effluents	0.7-5.93	93.45-120.0 ⁵	-5.47/0.1	-5.26/1.0
CN(F)	Microdiffusion, spectrophotometry	Reagent water	2.73-5.09	101.6-102.4	0.12	0.22
		5 effluents	0.0-12.3	90.5-121.9 ⁶	-1.72/1.12	-0.24/-2.96

¹ Values reported represent the range of precision and recovery achieved for NaCN or $K_2Ni(CN)_4$ to indicate the upper and lower bounds measured by these studies.

² The values are the minimum/maximum bias observed for the five contaminated water samples.

³ Two samples gave a negative (-) recovery with both analytes, which indicates that cyanide was formed in the analytical test.

⁴ The POTW clarifier sample could not be analyzed because of high sulfide content, which had not been identified by the sulfide screening test.

⁵The sample of manufactured gas plant groundwater gave negative recoveries for both analytes because of the high background cyanide concentration.

⁶The POTW clarifier effluent gave recoveries of 51.65 and 65.75% for both analytes, probably because of the presence of sulfide.

The WERF study showed that all of the analytical methods that were evaluated for simple cyanide had acceptable precision (as measured by relative standard deviation) for all of the samples analyzed. However, each of the methods had problems with recovery and bias for one or more of the contaminated water samples that were evaluated.

The reagent water recoveries for the EPA CN(T) method that relies on low power UV digestion was relatively poor at the 5 µg/L spiking level. The recoveries for these methods were even poorer for the contaminated water samples. Zheng, A. et.al. (2003) observed that the low recoveries may support the EPA's concern that UV digestion is not adequate for some wastewater matrices.

Method OIA-1677 (ligand exchange, flow injection, amperometry for CN(A)) gave the overall best combination of precision and recovery for simple cyanides of the methods tested by the WERF project. The method did exhibit a small, but consistent, positive bias for all samples analyzed. The POTW primary clarifier effluent sample could not be analyzed by Method OIA-1677 because it contained a high sulfide concentration that was not identified by the screening test and therefore the sample was not preserved with lead acetate/lead carbonate.

Both of the methods for CN(W) that were tested for the WERF study and the microdiffusion method for CN(F) gave results that were essentially equivalent to Method 1677 for most of the contaminated water matrices evaluated. However, each of these methods had one sample that contained sufficient interferences to the extent that bias and recovery were significantly poorer than was measured for the other samples. The CN(W) test had a problem with the manufactured gas plant site sample, which contained a high background concentration of cyanide. It is very difficult to measure small spike concentrations in such samples. The CN(F) test performance was adversely affected by the high sulfide concentration in the POTW primary effluent sample.

Standard Methods (APHA, 1999) and a few other references provide data on the precision and recoveries (or bias) achievable by these methods. However, these other references rarely have performance data for concentrations of cyanide below 20 µg/L, so they are of limited use. Table 10 summarizes the most relevant

cyanide performance data for methods that are relevant to this study.

Table 10
Additional Data on Precision and Recovery
of Simple Cyanide from Aqueous Matrices

Analyte	Method	Matrix	Spike (µg/L)	Relative Standard Deviation (%)	Recovery (%)	Reference
CN(T)	Distillation, spectrophotometry SM 4500-CN ⁻ E	Reagent water	60	16.8	100	APHA, 1999
		Wastewater	60	24.2	100	
	Distillation, spectrophotometry EPA 335.2	Wastewater	60	8.33	85	EPA, 1979
CN(A)	Chlorination, distillation, spectrophotometry, SM 4500-CN ⁻ G	Reagent water	8	41.2	112.5	APHA, 1999
		Wastewater	8	96.25	162.5	
CN(W)	Distillation, spectrophotometry, SM 4500-CN ⁻ I	Reagent water	30	29.7	100	APHA, 1999
		Wastewater	30	20.7	96.7	
	Distillation, ion-selective electrode, SM 4500-CN ⁻ I	Reagent water	30	19.7	100	
		Wastewater	30	16.0	100	
CN(F)	Microdiffusion, spectrophotometry	Reagent water	32	11.8	98.1	ASTM D 4282-02
		Mixed matrices	32	8	95.9	

The performance data in Table 10 should be viewed with some skepticism, given the high spiking levels that were used. However, one point that stands out is that the CN(A) method using chlorine (i.e., cyanide amenable to chlorination, CATC) performs very poorly at low concentrations, even in reagent water. The relative standard deviation of 96.26% reported in *Standard Methods* for wastewater matrices indicates that there is a probability of greater than 30% in any given sample that a measured value of CN(A) is over twice or less than one-half of the “true” value. In addition, the performance data show that the chlorine amenable cyanide method has a potentially strong positive bias (i.e., average recovery of 162.5%). This very poor performance is the reason why there has been an active search for alternatives to the cyanide amenable to chlorine analytical method.

Interferences

As stated in previous sections of this report, all of the available analytical methods for cyanide are subject to numerous interferences. Table 11 summarizes the most common interferences and controls and/or analytical methods that minimize the interference.

Table 11
Interferences in Analyses for Cyanide

Interference	Analyte	Method(s)	Corrective Action
Oxidizing agents (e.g., chlorine, ozone)	All CN species	All	Add ascorbic acid, sodium arsenite or sodium thiosulfate at time of collection
Sulfides and other sulfur compounds	All CN species	Distillation methods	Test sample for sulfide, if present add lead carbonate or lead acetate at time of collection. Lead carbonate powder is used when there is sufficient sulfide to cause a solution pH problem if lead acetate is used.
			Use ion chromatography to separate sulfides from distillate before colorimetric or amperometric detection
Nitrites/nitrates	CN(T), CN(A)	Distillation methods	Add sulfamic acid to the sample at time of collection.
Aldehydes, glucose and other sugars	All CN species	All	Stabilize with sodium hydroxide to pH 12-12.5 and add ethylenediamine solution
Unidentified organic compounds	CN(T), CN(A), CN(W)	Distillation methods	Use non-distillation method for simple cyanides (e.g., OIA-1677, ASTM 4282-02)

Standard Methods (APHA, 1999) describes most of the common interferences in the analytical methods for cyanide and how they may be corrected or minimized. However, research has shown that many of the interferences are not well understood and following the corrective action/preservation steps described in *Standard Methods* may not satisfactorily control the interferences in a specific sample matrix.

Sulfides and sulfur compounds that may convert to sulfides during the acid distillation step of the CN(T), CN(A) (chlorination), and CN(W) methods are one of the most common interferences. Sulfide causes a positive interference — more cyanide is reported than is present. Sulfides also interfere with the ligand exchange CN(A) (Method OIA-1677) method and the CN(F) (microdiffusion) method because they will measure as cyanide in both the amperometric and spectrophotometric detection methods. The addition of lead salts (at the time of collection) is the recommended method for controlling this interference. However, the sulfide screening procedure described in *Standard Methods*

(APHA, 1999) has been shown to be inadequate, indicating that no sulfide is present in a sample when in fact sufficient sulfide is present to interfere with the analysis (Zheng, A., et.al., 2003). The ion chromatography/amperometry method for analyzing the distillate has been used by some plants to control sulfur interference in the cyanide test (Matz, S.G., 1996). There are at least two plants in Texas that have had the ion chromatography/amperometry method approved as an alternate detection method for CN(T), CN(A), and CN(W).

Nitrites are another major interfering chemical in cyanide analyses. Nitrites are often present at low concentrations in effluents of treatment plants with biological nitrification. During periods of upset at such plants nitrite concentrations can increase to mg/L levels. In the distillation step of procedures that use this method of cyanide separation nitrite may react with organic compounds that are present in a wastewater sample to form cyanide, and are thus a positive interference (APHA, 1999). Addition of sulfamic acid to the sample is prescribed as a corrective measure.

Recent research has shown that nitrates, as well as nitrite, can react during distillation to form cyanide (Carr, S.A., Baird, R.B., and Lin, B.T., 1997). This 1997 study demonstrated significant formation of cyanide during the distillation step by the reaction of nitrites and nitrates with cellulose-derived and other natural organic substances commonly found in treated effluents. Ascorbic acid, which is an EPA-recommended preservative for cyanide, was shown to generate significant concentrations of cyanide when nitrites and nitrates were present in the wastewater. The research demonstrated that sulfamic acid successfully controlled nitrite-nitrate interferences, if it is spiked in samples at the recommended concentrations. The research also recommended that the sulfamic acid be spiked into the sample when it is collected to prevent pre-reflux reactions between nitrogen oxides and carbon compounds, which they believe may also occur.

Standard Methods (APHA, 1999) indicates that nitrite/nitrate interference does not occur in the CN(W) method (SM 4500-CN⁻I) because it is not performed under strong acid conditions.

Therefore, *Standard Methods* does not recommend adding sulfamic acid to samples that are to be analyzed for CN(W).

However, unpublished research by a POTW that treats a complex mixture of industrial wastewater and municipal sewage strongly indicates that the CN(W) method is subject to interference by nitrites. Therefore, it is prudent to add sulfamic acid to samples that will be analyzed for CN(W).

A study conducted by Research Triangle Institute for EPA evaluated the effects of multiple interferences in a wastewater sample and the effectiveness of corrective actions described in the methods (Goldberg, M., Clayton, A., and Potter, B.B., 1994). The study evaluated interferences due to sulfide, hypochlorite, formaldehyde, thiocyanate, and bisulfite in synthetic metal plating samples. They concluded the following:

- Interference recognition tests worked poorly when multiple interferences were present in a sample.
- Holding time between collection and analysis was important because of the reaction rates of the different interferences.
- The effect of each interference on individual analytical results was statistically significant even after application of the corrective method.

It is apparent from the method descriptions and articles in the scientific literature that cyanide analysis at trace concentrations (1-20 µg/L) can be subject to many matrix interferences, some of which can be controlled and some of which cannot. The interferences and their importance in terms of achieving reliable low-level cyanide measurements are matrix-specific with more complex matrices representing potentially greater difficulty. Some NPDES permittees have found that they must conduct a substantial amount of method development to obtain reliable data for NPDES permit compliance monitoring.

The only practical approach for assuring reliable trace level cyanide data for a particular effluent or surface water is to perform matrix spiking at low concentrations to determine the performance of the method (precision and recovery) being considered for use. If inadequate performance due to interferences occurs, then alternative corrective actions or analytical methods can be used to attempt to obtain reliable and consistent measurements.

Preliminary Treatment of Samples

The prescribed techniques for preservation and preliminary treatment of samples are as follows:

1. Add sodium hydroxide (NaOH) to raise pH to > 12.
2. Hold at 4 °C until analysis (maximum holding time 14 days)
3. Add ascorbic acid if residual chlorine is present (40 CFR 136, Table 2). *Standard Methods* (APHA, 1999)

recommends sodium arsenite or sodium thiosulfate as substitutes for ascorbic acid.

4. Screen sample for the presence of sulfides with lead acetate litmus paper.¹⁷ Add lead acetate or lead carbonate powder to react with sulfides. Particulate metals should be filtered from sample before adding lead salt (APHA, 1999).
5. Add sulfamic acid to the sample if nitrites/nitrates are expected to be present and the sample will be analyzed by a distillation method (APHA, 1999). Based on recent research, the sulfamic acid should be added in the field when the sample is collected.
6. If aldehydes or sugars are expected to be present in the sample, add ethylenediamine to the sample before distillation analysis (APHA, 1999).
7. If sulfite (SO_3^-) is present in the sample, titrate with hydrogen peroxide before analysis (APHA, 1999).

¹⁷ As noted above, this has step has been shown not to identify low concentrations of sulfide in wastewater samples that may interfere with the test.

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. Because of its toxicity to aquatic life, state and tribal water quality standards always include cyanide as a regulated pollutant.

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 µg/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.

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).

EPA criteria, and any state criteria derived from the EPA database, are based on free cyanide. Permittees should not accept water quality-based effluent limits (WQBEL) that are expressed as total cyanide [CN(T)], or that assume total cyanide is equivalent to free cyanide.

Petroleum industry wastewaters containing cyanide are generated only in the refining sector, and then only in a few processes. 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 cyanides.

Historically, the amount of cyanides in refinery wastewater has not been considered of regulatory concern because the typical refinery treatment processes (oil and solids separation, biological treatment) remove them efficiently. However, because the water quality-based effluent limits for cyanides may be very low for some refineries (i.e., < 20 µg/L), the ability of the available analytical methods to demonstrate compliance with NPDES permit limits is a continuing problem.

Analytical methods are available for measuring the cyanide compounds that are important in wastewater discharges and are regulated by water quality standards. The simple cyanides, the form of cyanide that most closely represents the free cyanide regulated by the EPA and state water quality criteria, can be measured by 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
- (3) Free cyanide [CN(F)], as defined by ASTM (Method D 4282-02).

The analytical 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 many matrix interferences present in wastewater. EPA Method 335.1 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 µg/L. This analytical method is acceptable for refinery effluent compliance testing and will minimize the potential of positive interferences.

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 µg/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. Both of these methods are recommended for NPDES permit compliance testing as they are minimally affected by the most common matrix interferences.

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 that are typical of water quality-based

effluent limits in some 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. 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 addition of sodium hydroxide to raise the sample pH to >12.0 (addition in the field);
- ▮ Immediate addition of sulfamic acid if the sample may contain nitrites and/or nitrates;
- ▮ 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 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.

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