Cyanide Compliance
Some Problems and Some Solutions

Regional Water Quality Control Board, Colorado River Basin Region
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Cyanide compliance has periodically become an issue for dischargers in Riverside and Imperial Counties. Cyanide compliance issues have been studied over the last years in Region 7 but known problems with sampling, sample preservation, holding times and analysis methods have not yet been resolved. We continue to see random cyanide "hits" in wastewater treatment plant discharges – discharges without any likely (or unlikely) source of cyanide to the collection system. Such false positive cyanide results are problematic. First, it is unclear whether there is an actual threat to the receiving water quality that needs to be addressed. Second, false positive results may compel the discharger to install expensive upgrades to control a pollutant discharge that may not exist. This white paper was written to address some of the uncertainties surrounding the validity of sample collection-, sample preservation- and analysis methods used today and propose steps that can be taken by the regulator and the discharger to find appropriate solutions that will ultimately reveal whether there is indeed a threat to water quality or if observances of cyanide in the wastewater effluent are "false" positives.

INTRODUCTION

Generally, cyanide is not found in municipal sewers unless cyanide or cyanide compounds have been illegally discharged. The absence of cyanide in municipal wastewaters was recognized by U.S. EPA when it removed cyanide from its economic analysis for the final CTR because EPA's analysis of data and facility information resulted in no reasonable potential for cyanide[1]. So, in the following we will assume that there is not a gold processing facility in the neighborhood and that the Discharger has implemented a robust source control program and ruled out any other potential cyanide sources that may end up in the collection system.

The objective of this White Paper is to:

- Discuss sources of cyanide;
- Provide an overview of cyanide speciation and toxicity;
- Summarize the latest findings on cyanide sampling and analysis;
- Review 40 Code of Federal Regulations (CFR) Part 136 May 12 2012; and
- Provide some ideas on how to proceed if you have "random" cyanide hits in your samples.

SOURCES OF CYANIDE

Man-made sources are responsible for much of the cyanide in the environment. Facilities where cyanides are produced or used include steel, electroplating, mining, and chemical industries, extraction of gold and silver ores, metal cleaning, manufacture of synthetic fibers, various plastics, dyes, pigments, and nylon, and as reagents in analytical chemistry. Cyanides are also used as insecticides and fumigants[2].

Most troubling for many dischargers is the fact that cyanide or cyanide-like compounds can also be created in the wastewater treatment process itself. There is substantial evidence in the published literature that indicates that analytical problems have resulted in the reporting of false positives, rather than the actual free cyanide

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[1] U.S. EPA (1999) "Comment ID: CTR-093-001", California Toxics Rule-Response to Comments Report, Volume 1.

[2] Agency for Toxic Substances and Disease Registry (ATSDR). (2006) "Toxicological Profile for Cyanide (Update)". Atlanta, GA: U.S. Department of Health and Human Services, Public Health Services. The primary source of cyanide in the air is from car exhaust. Other airborne sources include emissions from chemical processing, other industries, and municipal waste incinerators.

concentration in the treated wastewater effluent. For example, cyanide generation from precursors has been observed during disinfection (both chlorination and UV processes), as well as analytical interferences.[3,4] The interferences in cyanide analysis are complex and compounds such as sulfide, sulfur, aldehydes, sulfite, thiosulfate, thiocyanate, carbonate, nitrate, nitrite as well as other unknowns have been implicated for causing interferences with cyanide analysis[5]. Smoking is another important source of cyanide

In addition, sampling procedures for cyanide requires specific sample preservation protocols and holding times, which also have been implicated to generate “false” positives. Because wastewater effluent is a very complex solution it becomes extremely difficult (and cost prohibitive) to unravel the effect of specific or combinations wastewater effluent constituents on cyanide formation or destruction. Consequently, the uncertainties of cyanide analyses observed over twenty years ago still persist today.

CYANIDE SPECIATION

Cyanide, like many other chemical compounds, is found in different chemical forms or species. And, to make things even more complicated, different cyanide species are also defined by the analysis method used by the laboratory.

LABORATORY ANALYSIS “CYANIDE NAMES”

The most common species of cyanide are listed in Figure 1 and illustrates how the analysis method used by the laboratory also determines which of the cyanide species are accounted for[6].

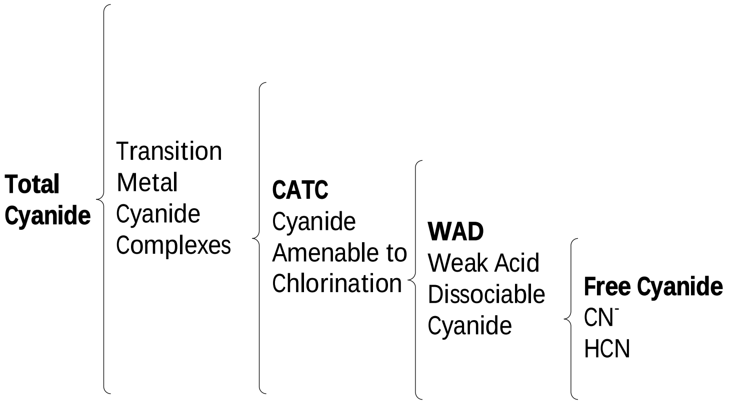

Figure 1. Cyanide speciation based on analysis method

Total Cyanide comprises the sum of all cyanide species present including cyanide-metal complexes that are very difficult to break up and the laboratory methods typically require strong acids and high temperatures to break

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[3] Giudice, Ben, D.; Jorgenson, Brant; Bryan, Michael (2011) “Problems Associated with Using Current EPA Approved Total Cyanide Analytical Methods for Determining Municipal Wastewater Treatment Plant NPDES Permit Compliance”, White Paper to CVRWQB, May 26, 2010 from Robertson-Bryan, Inc., Elk Grove, CA.

[4] Additional references can be found at the end of this White Paper.

[5] Telliard, William, A.; Sebroski, John (2009) “Development of Standard Practice D7365 for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide”, Presentation ASTM Committee D19 on Water Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water Cyanide Task Group, August 24, 2009.

[6] State Water Resources Control Board (SWRCB) Water Quality Enforcement Policy, May 20, 2010, identifies the following cyanide species in Table B: Cyanide (A); Cyanide and Thiocyanate–Total; Cyanide Complexed to Range of Compounds; Cyanide, Free Not Amenable to Chlorination; Cyanide in Bottom Deposits (dry weight); Cyanide Sludge Solid; Cyanide Filterable, Total; Cyanide, Free- Water plus Wastewaters; Cyanide Total (as CN); Cyanide, Total Recoverable; Cyanide, Weak Acid Dissociable; Cyanide, Dissolved (Std. Method); Cyanide, Free (Amenable to Chlorination).

these molecules apart before cyanide content can be measured. On the opposite end of the spectrum is Free Cyanide, which comprise cyanide in the ionic form, CN^-, and cyanide in molecular form, HCN. So when Total Cyanide, Cyanide Amenable to Chlorination (CATC), Weak Dissociable Acid Cyanide (WAD), or any other analysis method is used to determine compliance with a free cyanide effluent limitation, it should be clear that these methods will capture more forms of cyanide (if they are present) and are therefore would overestimate the toxicological threat to aquatic life.

OVERESTIMATING CYANIDE CONCENTRATIONS

One can argue that selecting an analysis method that captures more of the cyanide is a good idea in order to be on the "safe" side. The difficulty with this argument is that it is impossible to evaluate whether the safety factor is 1 or 10, or any other number for that matter, or even if receiving water quality is better protected. And to complicate matters, the more aggressive analysis methods that require harsh sample preservation techniques, high temperature distillation in strong acids, etc. are known to introduce "false" positive readings, e.g. readings that incorrectly indicate the presence of cyanide. Such false positives may prompt the discharger to engage in a vigorous toxicity source investigation, additional source control work, and potentially expensive plant upgrades when, in fact, there is no real threat to receiving water quality. An analogous situation is ammonia toxicity. When ammonia is an effluent discharge limitation, we typically require the discharger to monitor for ammonia (and pH) but not for Total or Kjeldahl nitrogen. To do so would in all likelihood overestimate the amount of ammonia in the effluent and also overestimate the risk to aquatic life due to ammonia toxicity.

FREE CYANIDE DISTRIBUTION

The toxicity of free cyanide, defined as the sum of molecular cyanide, HCN, and cyanide ion, CN^-, varies depending on its distribution, which is illustrated in Figure 2. In water, the distribution of HCN (red) and CN^- (white) depends upon pH. At near-neutral pH, CN^- is the predominant cyanide form in water while the toxic form, HCN, is comparatively small. Cyanide toxicity increases with increasing pH. At pH 8.3, which is not often exceeded in natural surface waters, only about 10 percent of any free cyanide occurs in the more toxic form as molecular cyanide, HCN.

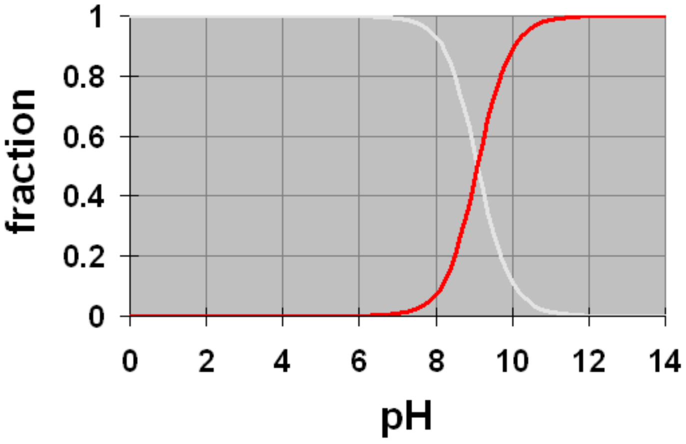

Figure 2. Distribution of CN- and HCN in water

So, when sampling for aquatic toxicity due to cyanide it is important to also have a measurement of the receiving water's pH[7] taken at the same time.

REGULATORY ISSUES

Up until 2012 United States EPA (U.S. EPA) approved[8] methods for cyanide only measured "total" cyanide or the sum of the more unstable cyanide species commonly known as "WAD" (weak acid-dissociable) cyanide. These methods typically overestimate the amount of free (toxic) cyanide in the sample and, hence, also the toxicological threat to aquatic environments. U.S. EPA has acknowledged the challenges of cyanide analysis and sample preservation and in May 2012 amended 40 CFR Part 136. To that effect, additional laboratory methods for free cyanide analysis were added to 40 CFR Part 136.

The currently approved methods for the analysis of free cyanide are listed in Table 1.

TABLE 1: Approved Methods for the Analysis of Free Cyanide in Aqueous Wastewater Effluents[9]

Method	Description
ASTM Standard Practice D7237-10	This method applies to free cyanide ions (HCN and CN-) and metal-cyanide complexes that dissociate into free cyanide at pH 6 to pH 8 in an aquatic environment are measured by this method using a Flow Injection Analysis (FIA) gas-diffusion technique with amperometric detection
OIA-1677-09	Samples are treated with a ligand exchange solution to liberate available cyanide which is introduced into an automated FIA system for measurement of the liberated cyanides using a gas diffusion technique coupled with amperometric detection.
ASTM Standard Practice D4282-02	This method relies on passive diffusion of cyanide at pH 6 and room Temperature. The sample is manually chlorinated with chloramine-T and subsequently reacted with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry.

The May 2012 amendment to 40 CFR Part 136 also revises the cyanide sample handling instructions and sample preservation procedures that are detailed in ASTM Standard Practice D7365-09a. Importantly, samples that are not analyzed within 15 minutes shall be preserved using sodium hydroxide pH>10 instead of previously at pH>12. The somewhat lower pH may alleviate the sample preservation problem previously discussed. The May 2012 revisions also include a more flexible approach to sample preservation and handling prior to laboratory analysis. The revisions allow "any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method". And importantly "Any removal or suppression technique not described in ASTM Standard Practice D7365-09a or the analytical test method must be documented along with supporting data". Specifically, D7365-09a provides explicit guidelines on eliminating sodium hydroxide as a preservative as part of the method.

In other words, the user can now conduct a hold-time/sample preservation study to evaluate whether the use of the sodium hydroxide preservative is indeed necessary. This is good news because it is now possible for a permittee to devise and conduct a controlled study to evaluate and assess preservation techniques, sample holding times, etc. in order to ensure that cyanide sample results are indeed representative. All approved cyanide analysis methods are listed in Table 2 for completeness.

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[7] The paired sampling of water quality and pH of the receiving water is also a requirement when monitoring for ammonia ($NH4^+$) toxicity.

[8] http://www.law.cornell.edu/cfr/text/40/136.3?qt-cfr_tabs=0#qt-cfr_tabs

[9] Currently, there is only one laboratory certified by the CDPH that performs analysis of free cyanide.

TABLE 2. List of Approved Inorganic Test Procedures (extracted from: http://www.law.cornell.edu/cfr/text/40/136.3?qt-cfr_tabs=0#qt-cfr_tabs)

Parameter	**Methodology** [58]	**EPA** [52]	**Standard methods**	**ASTM**	**USGS/AOAC/Other**
Cyanide—Total, mg/L	Automated UV digestion/distillation and Colorimetry				Kelada-01.[55]
	Segmented Flow Injection, In-Line Ultraviolet Digestion, followed by gas diffusion amperometry	-	-	D7511-09	-
	Manual distillation with $MgCl_2$, followed by any of the following:	335.4, Rev. 1.0 (1993) [57]	4500-CN−B-1999 or C-1999	D2036-09(A), D7284-08	10-204-00-1-X.[56]
	– Flow Injection, gas diffusion amperometry	-	-	D2036-09(A) D7284-08	-
	– Titrimetric	-	4500-CN−D-1999	D2036-09(A)	p. 22.[9]
	– Spectrophotometric, manual	-	4500-CN−E-1999	D2036-09(A)	I-3300-85.[2]
	– Semi-Automated [20]	335.4, Rev. 1.0 (1993) [57]	-	-	10-204-00-1-X,[56] I-4302-85.[2]
	– Ion Chromatography	-	-	D2036-09(A)	-
	– Ion Selective Electrode	-	4500-CN−F-1999	D2036-09(A)	-
Cyanide-Available, mg/L	Cyanide Amenable to Chlorination (CATC); Manual distillation with $MgCl_2$, followed by Titrimetric or Spectrophotometric	-	4500-CN−G-1999	D2036-09(B)	-
	Flow injection and ligand exchange, followed by gas diffusion amperometry[59]	-	-	D6888-09	OIA-1677-09.[44]
	Automated Distillation and Colorimetry (no UV digestion)	-	-	-	Kelada-01.[55]
Cyanide-Free, mg/L	Flow Injection, followed by gas diffusion amperometry	-	-	D7237-10	OIA-1677-09.[44]
	Manual micro-diffusion and colorimetry	-	-	D4282-02	

Note: For footnotes in Table 1B go to: http://www.law.cornell.edu/cfr/text/40/136.3?qt-cfr_tabs=0#qt-cfr_tabs

MITIGATION STRATEGIES

There are a number of possible mitigation strategies that can be employed, single or multiple, to help ensure that cyanide sample results are representative of actual cyanide concentrations in the wastewater effluent. It is important for both the discharger and the regulatory agencies that under- and/or overestimating cyanide concentrations in wastewater effluent is avoided so that receiving water quality is protected.

We have listed four areas of investigation, or strategies, in no particular order that a Discharger could pursue if cyanide is found in the effluent sample.

STRATEGY 1: SOURCE CONTROL

If sample result(s) come back positive for cyanide, a source control program should be implemented to identify or rule out any of the more obvious sources of cyanide. For example, the Discharger should verify if any of the following commercial or industrial sources are discharging to the collection system:

- Gold mine and/or ore processing facility,
- Artist's photography studio – sepia toning,
- Metal/chrome plating facility w. discharge to sewer,
- Pest exterminator using cyanide gas,
- Laboratory using reagents containing cyanide, or
- Facility producing nylon or plastics

A brief survey is readily performed by checking with the Regional Board, County Environmental Health Department, City, or County business licenses, yellow Pages, etc. Depending upon the findings, the Discharger should then continue the investigation to identify the ultimate cyanide source or proceed with an alternative strategy. In either case, the methodology used for conducting the source control study and the outcome of the study should be well documented.

STRATEGY 2: SELECT APPROPRIATE CYANIDE ANALYSIS

If monitoring indicates cyanide exceedances and if the cyanide analysis employed by the laboratory is either total or "available" cyanide then the permit holders could conduct an additional analysis specific for free cyanide using the same, e.g. split, sample. In all cases, it is good practice to collect a sample large enough so that a "split" sample is kept at the discharger's facility. If there is an exceedance then the discharger has the option to send the "split" sample to the same laboratory (or a different laboratory) for confirmation. The key is to submit a sample to the laboratory early enough in the reporting period to allow for sufficient time to conduct additional sampling/analysis if needed.

Today[10], there is only one laboratory in California that is certified to perform free cyanide analysis, namely WECK Laboratories, located in City of Industry. E.S. Babcock and Sons Laboratories, in Riverside, has submitted an application for certification to conduct free cyanide analysis and a formal approval is expected in the near future.

STRATEGY 3: CONTROLLED STUDY PER ASTM STANDARD PRACTICE D7365-09A

Dischargers can now conduct controlled studies of any interference removal or suppression techniques, including techniques that are not described in ASTM Standard Practice D7365-09a or in the description of the analytical test

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[10] September 2, 2014.

method. For example, the permittee can devise a controlled study in collaboration with an analytical laboratory with the goal to ensure that cyanide sample results are valid. For example, parameters that may be included in such a study are: cyanide analysis protocol, holding time, preservation techniques using sodium hydroxide at different pH values, keeping the sample chilled or even frozen, etc.

STRATEGY 4: MULTIPLE SAMPLES COLLECTED IN ONE DAY

To minimize the risk associated with collecting only one grab sample it may be advantageous to collect multiple grab samples at different times throughout the day. This, to better assess whether cyanide is present or not in the wastewater effluent, and if so, multiple grab samples will provide a more representative estimate if there is an actual threat to water quality.

Using multiple daily grab samples:

Here we are using 4.3 µg/L as the effluent limitation using Order R7-2014-0004 NPDES No. CA7000009, Waste Discharge Requirements for City of Calexico Water Pollution Control Plant City of Calexico as the example. The sampling event envisioned here is as follows:

1. Collect three grab samples during the day - one grab sample in the morning, one mid-day, and the third grab sample in the afternoon.
2. Send one sample to the laboratory and analyze for cyanide[11] and store[12] the others until needed.
3. If the result for the first sample comes back indicating that cyanide concentration exceeds the limit, submit the next sample to the lab for analysis, and so on.

Data are interpreted as follows[13]:

Sample 1: The result from Sample 1 is 42 µg/L.

Obviously, this is much larger than the effluent discharge limit of 4.3 µg/L and the Discharger is not in compliance. And, we now send Sample 2 to the laboratory for analysis.

Sample 2: The result from Sample 2 is 2.5 µg/L.

This is less than the effluent limitation and "When determining compliance with an AMEL or MDEL for priority pollutants and more than one sample result is available, the Discharger shall compute the arithmetic mean …".

Example Data set	Arithmetic Mean
Sample 1 = 42 µg/L	(42 µg/L + 2.5 µg/L)/2 = 21.3 µg/L
Sample 2 = 2.5 µg/L	**Answer: 21.3 µg/L > 4.3 µg/L Discharger is not in compliance**

Now the arithmetic mean is 21.3 µg/L for the two samples, which is larger than 4.3 µg/L and the Discharger is still not in compliance. Since the result of the second sample was below the effluent limitation there is a possibility that the first sample is an anomaly and we send Sample 3 to the laboratory for analysis.

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[11] Using the method of analysis required in the permit and complement, if so desired, with any other method

[12] Go to Strategy 2 if storage and preservation method is different than the prescribed.

[13] The methodology for determining compliance is from the "Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California (SIP)", see p. 26, Section 2.4.5 *Compliance Determination*.

Sample 3: The result from Sample 3 is Non Detect (ND).

Now, since one of the samples is "Non Detect" ND, or "Detected, but Not Quantified" (DNQ), then the compliance determination relies on the median value and not the arithmetic mean of the three samples collected during the one day.

The procedure to determine compliance when we have a ND and/or DNQ is as follows:

a. Rank data from low to high – noting that the order of NDs and DNQs is unimportant.
b. Determine Median Value.

Example Data set	Ranking
Sample 1 = 42 µg/L	ND : **2.5 µg/L** : 42 µg/L
Sample 2 = 2.5 µg/L	"Median" or "middle" value is 2.5 µg/L. and
Sample 3 = ND	**Answer: 2.5 µg/L < 4.3 µg/L Discharger is in compliance**

If there are an odd number of samples then the median is the middle value, which in our case for three samples is ND. However, if there are an even number of samples then the median value is calculated by taking the average of the two "middle" values. And, if one of the "middle" values is ND or DNQ then the average will also be ND or DNQ.

So, by collecting multiple grab samples at different times throughout the day, we can obtain a more representative sample, which in turn will allow us to better assess whether cyanide is present or not in the wastewater effluent and if the threat to receiving water quality is real or not..

ADDITIONAL REFERENCES

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