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(CAS #: 57-12-5)

This memo clarifies how cyanide concentrations in effluent and surface water are measured to determine compliance with water quality criteria.

Criteria Summary

Oregon water quality standards include numeric criteria for cyanide to protect human health and aquatic life. Criteria for human health are expressed as total cyanide, while criteria for aquatic life are expressed as free cyanide (See table below).

Chemical	Species	Human Health Criteria		Aquatic Life Criteria (Freshwater)		Aquatic Life Criteria (Saltwater)	
		Water + Org (µg/L)	Org Only (µg/L)	Acute (µg/L)	Chronic (µg/L)	Acute (µg/L)	Chronic (µg/L)
Cyanide	total cyanide	130 ^G	130 ^G				
Cyanide	free cyanide			22 ^J	5.2 ^J	1 ^J	1 ^J

^GThe cyanide criterion is expressed as total cyanide (CN)/L.
^JThis criterion is expressed as µg free cyanide (CN)/L.

Key Issues

Human health and aquatic life criteria for cyanide were developed based on cyanide's toxicity to humans (total cyanide) and aquatic life (free cyanide).

Free cyanide is defined as the sum of the cyanide present as hydrogen cyanide (HCN) and as the cyanide ion (CN⁻) and is dependent on pH and temperature.¹ Free cyanide is a more reliable measure of toxicity to aquatic life than total cyanide because total cyanide can include nitriles and other stable metalocyanide complexes that are not very toxic to aquatic life.² EPA recently approved methods for free cyanide and preliminary research indicates that these analytical costs are more expensive than the analysis for total cyanide.

¹ EPA. Ambient Water Quality Criteria for Cyanide. EPA 440/5-84-028. January 1985. See: <http://nepis.epa.gov/EPA/html/DLwait.htm?url=/Exe/ZyPDF.cgi?Dockkey=P1002W79.PDF>

² *Ibid.*

Most facilities are required to monitor for total cyanide as part of Tier 1 priority pollutant screening (40 CFR 122). To determine compliance with cyanide criteria, DEQ's current practice is to compare total cyanide data results to the criteria for aquatic life (free) and human health (total). However, this approach results in an overly conservative assessment of compliance with aquatic life criteria, which are based on free cyanide.

Recommended Analytical Methods

Total cyanide methods rely on analysis after distillation. The cyanide concentration is determined with titration, ion chromatography, colorimetric procedure (spectrophotometric), selective ion electrode, or flow injection analysis with gas diffusion separation and amperometric detection. EPA recommends EPA 335.2, 335.3, 335.4 and methods SM 4500-CN C, D, E, and F published in the *Standard Methods for the Examination of Water and Wastewater*. Method ASTM D6888-04 is an additional approved method for analysis of total cyanide.

EPA has approved three methods for free cyanide; OIA 1677-09, ASTM method D4282-02 and ASTM method D7237-10. The analyses for free cyanide by these new methods are available at a limited number of laboratories because they utilize relatively new technology. It should be noted that the costs for analysis of free cyanide is more expensive relative to the analysis of other forms of cyanide.

Additionally, there are two other cyanide forms that are commonly tested in lieu of free cyanide. Cyanide Amenable to Chlorination (CAC) is analyzed by SM 4500-CN G and is approved by EPA for NPDES compliance. The other is Weak Acid Dissociable (WAD) cyanide (SM 4500CN I). Although the WAD analytical method for cyanide is not EPA approved, it is used by many labs. The CAC and WAD methods are used to determine "available" cyanide (free cyanide plus easily dissociated forms) and thus do not produce results equivalent to total cyanide. These methods however, could still feasibly be used as a surrogate method for free cyanide in the same way total cyanide may be used. The CAC and WAD methods however, could not be used as a replacement for the total cyanide methods.

To determine the applicable quantitation limits for individual permit holders, please refer to Schedule B of the applicable permit. For older permits without quantitation limits in their Schedule B, please refer to Revision 3.0 of the [Reasonable Potential Analysis for Toxic Pollutants IMD](#) to determine applicable quantitation limits.

Implementation Instructions for NPDES Permits

Option 1: Total cyanide data may be used as a surrogate measurement for free cyanide in Tier I monitoring and reasonable potential analysis (RPA) requirements. This allows the permit holder to minimize sampling costs. Total cyanide results must then be entered into the RPA Workbook and used to determine if cyanide is a Pollutant of Concern. In the event of an affirmative finding, DEQ recommends that the permit holder conduct an analysis specific for free cyanide as part of the Tier 2 monitoring.

Option 2: Total cyanide or "available" cyanide data may be used as a surrogate measurement for free cyanide in Tier 1 monitoring and RPA and for calculating an effluent limit, if applicable. This will result in a more conservative analysis for the aquatic life criteria.

Option 3: Conduct monitoring for both total cyanide and free cyanide during Tier 1 monitoring

and RPA and for calculating an effluent limit, if applicable.

Conclusion

Total or “available” cyanide data may be used as a conservative surrogate for free cyanide in cases where there are no analytical results based on free cyanide. DEQ recommends that permit holders conduct an additional analysis specific for free cyanide for a Tier 2 analysis if Tier 1 monitoring indicates that cyanide is a Pollutant of Concern.