

To: DEQ Water Quality Staff

From: Water Quality Permitting and Program Development

Date: April 12th, 2022

Updated By: Aliana Britson, *Water Quality Permitting and Program Development (4/12/2022)*

Subject: Implementation Instructions for Free and Total Cyanide Water Quality Criteria (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.
^J This 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 metallo-cyanide complexes that are not very toxic to aquatic life.¹

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>

Depending on size and type, some NPDES individual permits that have domestic and industrial discharges are required to monitor for total cyanide and free cyanide (40 CFR 122). To determine compliance with cyanide criteria, DEQ's current practice is to compare total cyanide data results to the human health criterion and free cyanide with the aquatic life criterion. In the absence of free cyanide data, total cyanide may be used as a conservative assessment for compliance with the aquatic life criterion.

Recommended Analytical Methods

EPA has approved a number of analytical methods for both Total and Free Cyanide that can be found in 40 CFR 136, table IB "List of Approved Inorganic Test Procedures".

Additionally, there are two other cyanide forms that are commonly tested in lieu of free cyanide. Cyanide Amenable to Chlorination (CAC), also known as "Available Cyanide" is analyzed by SM 4500-CN G and is a 40 CFR 136 approved method for Available Cyanide. 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 may not produce results equivalent to total cyanide. The CAC and WAD methods cannot be used as a replacement for the total cyanide methods. These methods however may be used as a surrogate method for free cyanide in the event that no free cyanide data is available.

Implementation Instructions for NPDES Permits

Total cyanide data may be used as a conservative surrogate to complete a reasonable potential analysis (RPA) if no free cyanide data is available at the time of permit renewal. Any WQBELs calculated using total cyanide must be reviewed by the RPA subject matter expert and/or direct support. If cyanide is identified as a pollutant of concern, monitoring for both total and free cyanide results must be included in the renewed permit.

Conclusion

Monitoring for total and free cyanide results are required in cases where monitoring for cyanide would be required. Total cyanide results may be used as a conservative surrogate in cases where there are no analytical results for free cyanide in order to complete the RPA.