MO DNR DEQ WPP Permit Writer's Manual Topic
Ch. 6 Monitoring and Reporting Requirements
6.1.5.4 Monitoring Conditions / Other Considerations / Analytical Detection Levels
Cyanide Amenable to Chlorination

Applicability:
Determining compliance levels for NPDES permits when the Cyanide Amenable to Chlorination permit limit is not quantifiable using the standard EPA approved methods.

Background:
The Missouri Water Quality Standard for Cyanide, Amenable to Chlorination (herein after "CATC") is low (Acute 22 µg/L, Chronic 5 µg/L), resulting in some facility permits containing very low effluent limits. When using the most common and practical approved methods, these low limits cannot be measured with an accuracy acceptable for reporting purposes. A review of these methods finds they do not specify a method detection limit (MDL) which would be an easy way to calculate the minimum level (ML) department staff can use for compliance purposes. Figure 1. lists the most common species of cyanide as applied to wastewater.

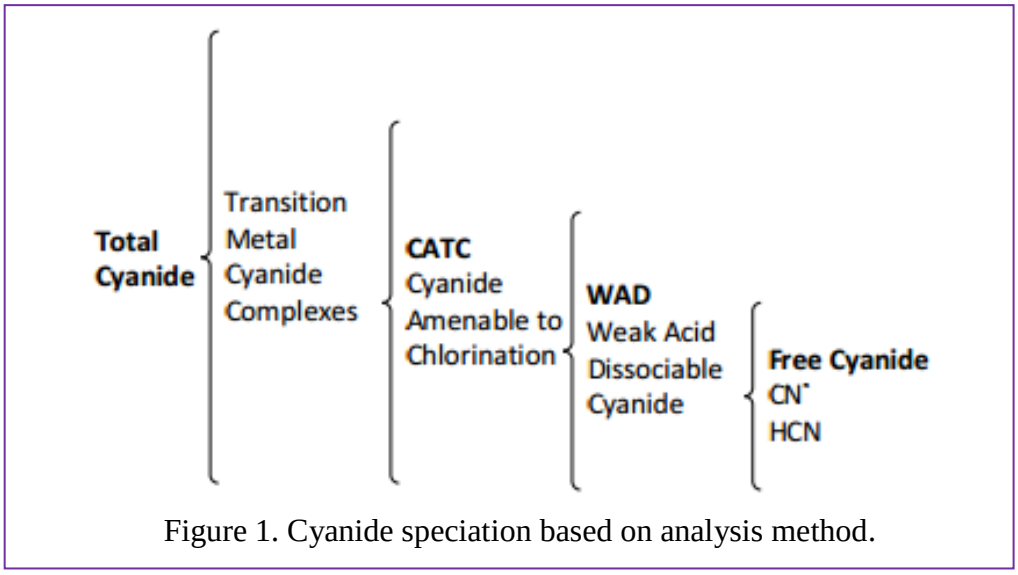

Figure 1. Cyanide speciation based on analysis method.

Total cyanide comprises the sum of all cyanide species present beginning with strongly complexed cyanide-metal complexes, moving to cyanide amenable to chlorination, then weakly associated cyanide complexes and ending with free cyanide. Weak cyanide complexes include zinc, nickel, copper, or cadmium complexes, and strongly complexed cyanides are cobalt and iron. It is advantageous to differentiate between total cyanide and cyanides amenable to chlorination as the CATC is more ecologically available. Cyanide compounds that are amenable to chlorination include free cyanide as well as those complex cyanides that are potentially dissociable (weak complexes) and therefore, potentially toxic at low concentrations.

Until 2012, the United States EPA (U.S. EPA) approved methods for cyanides only measured total cyanides or weak acid-dissociable (WAD) cyanide, a relatively unstable species. These methods typically overestimated or underestimated the amount of cyanide present and subsequent 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 include additional laboratory methods for available cyanide analysis. Currently, only two methods are approved to analyze and report for CATC and are found in the table below; Missouri water quality standards are written for only CATC.

40 CFR 136: TABLE IB—LIST OF APPROVED INORGANIC TEST PROCEDURES (AS AMENDED 2012)

Parameter	Methodology	EPA	Standard methods	ASTM	USGS/AOAC/ Other
Cyanide-Available, mg/L	Cyanide Amenable to Chlorination (CATC); Manual distillation with $MgCl_2$, followed by Titrimetric or Spectrophotometric	none	4500-CN^- G-1999	D2036-09(B)	none

Minimum Level of Quantification Determination:
The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. Relatedly, the Practical Quantitation Limit (PQL) is the lowest level of detection that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions.

The department's Environmental Services Program Laboratory performs CATC analysis using SM 4500-CN^- G. The laboratory method detection limit (MDL) is 3 µg/L and the Practical Quantitation Limit (PQL) is 10 µg/L, meaning the laboratory is capable of detecting CATC in effluent as low as 3 µg/L but due to variances in effluent characteristics, are only confident in levels of CATC detected at 10 µg/L or above.

The previous ML for available cyanide of 16 µg/L was based on EPA method 335.4. This method is no longer appropriate to determine CATC. Currently, Standard Method 4500-CN-G is the most practical method for analysis of CATC, however no published minimum detection limit (MDL) exists. The MDL of a particular method is always lower than the ML. For purposes of assessing compliance with permit limits, the ML has been determined to be 10 µg/L in accordance with Federal Register Vol. 60. #101; May 25, 1995 using the following calculations: 3 * 3.18 = 9.54 ≈ 10 µg/L. The derived ML and the laboratory PQL are equivalent therefore the ML is valid and appropriate.

Permit Language:
Permit writers will determine the appropriate CATC effluent limit for each facility. If the determined effluent limit is greater than or equal to 10 µg/L, it will be included in the permit as the CATC effluent limit for the facility. If the determined effluent limit is less than 10 µg/L, then the permit limit, the ML and the specified analytical method should be placed in the permit as follows:

Parameter	Units	Effluent Limit
Cyanide Amenable to Chlorination; CATC (Note 1)	µg/L	effluent limit value (ML10)

Note 1: This effluent limit is below the minimum quantification level (ML) of the most common and practical EPA approved methods. The department has determined the current acceptable ML for Cyanide Amenable to Chlorination (CATC) to be 10 µg/L when using SM 4500-CN^- G. Cyanides Amenable to Chlorination after Distillation in *Standard Methods for the Examination of Water and Wastewater*, 22nd Edition. The permittee will conduct analyses in accordance with this method, or equivalent, and report actual analytical values. Measured values equal to or greater than the minimum quantification level of 10 µg/L will be considered violations of the permit and values less than the minimum quantification level of 10 µg/L will be considered to be in compliance with the permit limitation. The minimum quantification level does not authorize the discharge of CATC in excess of the effluent limits as stated in the permit.

References/Links:
- Effluent Regulations - General Conditions - Monitoring, Analysis and Reporting 10 CSR 20-7.015(9)(D)
  - 40 CFR Part 136 Table IB: List of approved Inorganic Test Procedures {Link }

- 40 CFR Part 136 Appendix B: Guidelines Establishing Test Procedures for the Analysis of Pollutants-Definition and Procedure for the Determination of the Method Detection Limit {Link}
- *Technical Support Document for Water-Quality Based Toxics Control* (EPA/505/2-90-001), section 5.7.3
- *Determining Compliance With Water Quality Based Effluent Limits Below Quantitation in the Absence of Promulgated Minimum Levels (MLs)*, Federal Register: May 25, 1995 (Volume 60, Number 101) http://www.gpo.gov/fdsys/pkg/FR-1995-05-25/pdf/95-12894.pdf
- *Standard Methods for the Examination of Waters and Wastewater*, 22nd edition, Section 4500. American Public Health Association, 800 I Street NW, Washington, DC, 20001-3710

Key Words:
Cyanide Amenable to Chlorination, CATC, compliance level, detection level, minimum level of quantification (ML), minimum level, method detection limit (MDL)

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