Cyanide Clarification of Free and Total Cyanide Analysis for Safe Drinking Water Act (SDWA) Compliance

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Chemical Phase Rule V

57 FR 31776-31849 Chemical Phase Rule V (Vol. 57, No. 138, July 17, 1992) – States the following: Total cyanide methods are allowed for screening, the Maximum Contaminant Level (MCL)/Maximum Contaminant Level Goal (MCLG) applies to free cyanide, the agency definition of "free" is amenable to chlorination, and the MCL and MCLG is 0.2 ppm (mg/L).

- Cyanide is regulated as Free Cyanide (Table in 40 CFR 141.62(b) defines an MCL of 0.2 mg/L for Cyanide (as free cyanide)), but Total Cyanide methods are allowed for screening. The Total Cyanide screening methods are easier, faster and cheaper than the Free Cyanide methods.
    - If the total cyanide is <0.2 mg CN^-/L, you can report free cyanide as <0.2 mg/L;
    - If the total cyanide is ≥0.2 mg CN^-/L, determine free cyanide by an approved free cyanide method.
- The Agency has regulated FREE CYANIDE as Cyanides Amenable to Chlorination, and set the MCL based on Free Cyanide.
- Cyanides amenable to chlorination provides a conservative estimate of toxicity because, in addition to free cyanide, it recovers some weak acid dissociable metal cyanide complexes that may or may not actually release free cyanide in the environment.

Note: A good resource for definitions of cyanide terms can be found in ASTM D 6696-05.

Certification/Accreditation

The methods for free and total cyanide are listed in Table 40 CFR 141.23 (k)(1). Only the approved methods may be used:

> *Analysis for the following contaminants shall be conducted in accordance with the methods in the following table, or the alternative methods listed in appendix A to subpart C of this part, or their equivalent as determined by EPA…*

Free and total cyanide are part of the National Primary Drinking Water Regulations (NPDWRs) and 40 CFR 141.23 is referenced in 40 CFR 141.28(a) stating that laboratories analyzing compliance samples must be certified/accredited as follows:

> *For the purpose of determining compliance with §141.21 through 141.27, 141.30, 141.40, 141.74, 141.89 and 141.402, samples may be considered only if they have been analyzed by a laboratory certified by the State…*

Preservation

Excerpt from Table in 40 CFR 141.23 (k)(2)

Contaminant	Preservative[1]	Container[2]	Time[3]
Cyanide	4 °C, NaOH	P or G	14 days

[1] For cyanide determinations samples must be adjusted with sodium hydroxide to pH 12 at the time of collection. When chilling is indicated the sample must be shipped and stored at 4 °C or less …

[2] P = plastic, hard or soft; G=glass, hard or soft.

[3] In all cases samples should be analyzed as soon after collection as possible. Follow additional (if any) information on preservation, containers or holding times that is specified in method.

Summary:	Container:	Plastic or Glass
	Preservation:	NaOH to pH 12
		4 ˚C
	Holding Time:	14 days

Water Treatment and Cyanide

The oxidative effects of disinfection (chlorination and/or most of the alternatives like ozone, chlorine dioxide, etc…) can chemically alter the sample matrix and these oxidants may react with regulated contaminants. This isn't limited to contaminants like cyanide and glyphosate. Disinfection is an integral component of treatment, primarily to control microbial contaminants, but regulated contaminants may also be removed as a secondary benefit. Other forms of treatment like aeration or Granular Activated Carbon (GAC) are specifically designed to remove regulated organic chemicals, and even though these treatments are used, the Public Water System (PWS) must still monitor for those contaminants. Contaminants like cyanide (and glyphosate) are no different. The statements in some methods regarding disinfectant reactivity with certain contaminants are typically included in those methods to assist laboratories and PWSs with interpreting data, not to grant any allowance to the PWS to forgo monitoring because of the expectation that the contaminant will no longer be measured in the treated water. For example, microbial monitoring must still occur on the finished water even though the source water is treated with chlorine as a disinfectant.

PE Acceptance Limits

The Table in 40 CFR 141.23 (k)(3)(ii) (excerpt shown below) lists the Performance Evaluation (PE) Acceptance Limit for Cyanide as ± 25% at ≥0.1 mg/L.

Excerpt from Table in 40 CFR 141.23 (k)(3)(ii)

Contaminant	Acceptance Limit
Cyanide	± 25% at ≥0.1 mg/L

Maximum Contaminant Level (MCL)

The Table in 40 CFR 141.62 (b) (excerpt shown below) lists a Maximum Contaminant Level (MCL) of 0.2 mg/L for Cyanide (as free Cyanide). Cyanide is therefore regulated as free cyanide.

Excerpt from Table in 40 CFR 141.62 (b)

Contaminant	MCL (mg/L)
(13) Cyanide (as free Cyanide)	0.2

Methodology

Methodologies for Cyanide are shown in Tables in 40 CFR 141.23 (a)(4)(i), 40 CFR 141.23 (k)(1) and Appendix A to Subpart C of Part 141. Excerpts from these Tables are shown below.

Excerpt from Table in 40 CFR 141.23 (a)(4)(i)

Contaminant	MCL (mg/L)	Methodology	Detection limit (mg/L)
Cyanide	0.2	Distillation, Spectrophotometric[3]	0.02
		Distillation, Automated, Spectrophotometric[3]	0.005
		Distillation, Amenable, Spectrophotometric[4]	0.02
		Distillation, Selective Electrode[3 4]	0.05
		UV, Distillation, Spectrophotometric[9]	0.0005
		Micro Distillation, Flow Injection, Spectrophotometric[3]	0.0006
		Ligand Exchange with Amperometry[4]	0.0005

[3] Screening method for total cyanides.
[4] Measures "free" cyanides when distillation, digestion, or ligand exchange is omitted.
[9] Measures total cyanides when UV-digestor [*sic*] is used, and "free" cyanides when UV-digestor [*sic*] is bypassed.

[Note: This table is primarily used in conjunction with Consumer Confidence Reports.]

The Table in 40 CFR 141.23 (a)(4)(i) has several footnotes that indicate:

- Screening methods for total cyanides have footnote 3.
- Free cyanide methods – with distillation, digestion or ligand exchange omitted – are indicated by footnote 4.
- There is one methodology associated with both footnotes 3 and 4 so it can be used to measure both free and total cyanides.
- UV, Distillation, Spectrophotometric, footnote 9, is also approved to measure free and total cyanides. It measures total cyanides when the UV-digester is used and free cyanides when the UV-digester is bypassed.

Excerpt from Table in 40 CFR 141.23 (k)(1)

Contaminant	Methodology[13]	EPA	ASTM[3]	SM[4] (18th, 19th ed.)	SM[4] (20th ed.)	SM Online[22]	Other
12. Cyanide	Manual Distillation followed by		D2036-98 A	4500-CN^- C	4500-CN^- C		
	Spectrophotometric, Amenable		D2036-98 B	4500-CN^- G	4500-CN^- G	4500-CN^- G-99	
	Spectrophotometric [*sic*] Manual		D2036-98 A	4500-CN^- E	4500-CN^- E	4500-CN^- E-99	I-3300-85[5]
	Spectrophotometric [*sic*] Semi-automated	335.4[6]					
	Selective Electrode			4500-CN^- F	4500-CN^- F	4500-CN^- F-99	
	UV, Distillation, Spectrophotometric						Kelada-01[17]
	Micro Distillation, Flow Injection, Spectrophotometric						QuikChem 10-204-00-1-X[18]
	Ligand Exchange and Amperometry[21]		D6888-04				OIA-1677, DW[20]

[3] Annual Book of ASTM Standards, ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428, http://www.astm.org.; Annual Book of ASTM Standards 1994, Vols. 11.01 and 11.02; Annual Book of ASTM Standards 1996, Vols. 11.01 and 11.02; Annual Book of ASTM Standards 1999, Vols. 11.01 and 11.02; Annual Book of ASTM Standards 2003, Vols. 11.01 and 11.02.

[4] Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 800 I Street NW., Washington, DC 20001-3710; Standard Methods for the Examination of Water and Wastewater, 18th edition (1992); Standard Methods for the Examination of Water and Wastewater, 19th edition (1995); Standard Methods for the Examination of Water and Wastewater, 20th edition (1998).The following methods from this edition cannot be used: 3111 B, 3111 D, 3113 B, and 3114 B.

[5] U.S. Geological Survey, Federal Center, Box 25286, Denver, CO 80225-0425; Methods for Analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of Inorganic and Organic Constituents in Water and Fluvial Sediment, Open File Report 93-125, 1993; Techniques of Water Resources Investigation of the U.S. Geological Survey, Book 5, Chapter A-1, 3rd edition, 1989.

[6] "Methods for the Determination of Inorganic Substances in Environmental Samples," EPA/600/R-93/100, August 1993. Available as Technical Report PB94-120821 at National Technical Information Service (NTIS), 5301 Shawnee Road, Alexandria, VA 22312. http://www.ntis.gov.

[13] ...

[17] The description for the Kelada-01 Method, "Kelada Automated Test Methods for Total Cyanide, Acid Dissociable Cyanide, And Thiocyanate," Revision 1.2, August 2001, EPA # 821-B-01-009 for cyanide is available from the National Technical Information Service (NTIS), PB 2001-108275, 5285 Port Royal Road, Springfield, VA 22161. The toll free telephone number is 800-553-6847. Note: A 450-W UV lamp may be used in this method instead of the 550-W lamp specified if it provides performance within the quality control (QC) acceptance criteria of the method in a given instrument. Similarly, modified flow cell configurations and flow conditions may be used in the method, provided that the QC acceptance criteria are met.

[18] The description for the QuikChem Method 10-204-00-1-X, "Digestion and distillation of total cyanide in drinking and wastewaters using MICRO DIST and determination of cyanide by flow injection analysis," Revision 2.1, November 30, 2000, for cyanide is available from Lachat Instruments, 6645 W. Mill Rd., Milwaukee, WI 53218. Telephone: 414-358-4200.

[20] Method OIA-1677, DW "Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry," January 2004. EPA-821-R-04-001, Available from ALPKEM, A Division of OI Analytical, P.O. Box 9010, College Station, TX 77842-9010.

[21] Sulfide levels below those detected using lead acetate paper may produce positive method interferences. Test samples using a more sensitive sulfide method to determine if a sulfide interference is present, and treat samples accordingly.

[22] Standard Methods Online, American Public Health Association, 800 I Street NW., Washington, DC 20001, available at http://www.standardmethods.org. The year in which each method was approved by the Standard Methods Committee is designated by the last two digits in the method number. The methods listed are the only online versions that may be used.

Excerpt from Table in Appendix A to Subpart C of Part 141

Contaminant	**Methodology**	**EPA method**	**SM 21st edition[1]**	**SM 22nd edition[28]**	**SM online[3]**	**ASTM[4]**	**Other**
Cyanide	Manual Distillation followed by					D2036-06 A	
	Spectrophotometric, Amenable		4500-CN^- G	4500-CN^- G		D2036-06 B	
	Spectrophotometric Manual		4500-CN^- E	4500-CN^- E		D2036-06 A	
	Selective Electrode		4500-CN^- F	4500-CN^- F			
	Headspace Gas Chromatography/Mass Spectrometry						ME355.01[7]

[1] Standard Methods for the Examination of Water and Wastewater, 21st edition (2005). Available from American Public Health Association, 800 I Street, NW., Washington, DC 20001-3710.

[3] Standard Methods Online are available at http://www.standardmethods.org. The year in which each method was approved by the Standard Methods Committee is designated by the last two digits in the method number. The methods listed are the only online versions that may be used.

[4] Available from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959 or http://astm.org. The methods listed are the only alternative versions that may be used.

[7] Method ME355.01, Revision 1.0. "Determination of Cyanide in Drinking Water by GC/MS Headspace," May 26, 2009. Available at http://www.nemi.gov or from James Eaton, H & E Testing Laboratory, 221 State Street, Augusta, ME 04333. (207) 287-2727.

[28] Standard Methods for the Examination of Water and Wastewater, 22nd edition (2012). Available from American Public Health Association, 800 I Street NW., Washington, DC 20001-3710.

Matching up the Methodologies in the cyanide entry in the Table at 40 CFR 141.23(a)(4)(i) with the methods in the cyanide entries in the Tables at 40 CFR 141.23 (k)(1) & Appendix A to Subpart C of Part 141, the methods approved for free cyanides, total cyanides, and/or both can be determined.

Modified Methodologies and Methods for Total and Free Cyanide Table

Contaminant	Methodology	EPA	ASTM	SM (18th, 19th, 20th ed.)	SM (21st, 22nd ed.)	SM Online	Other
12. Cyanide	*Manual Distillation followed by*		*D2036-98 A, -06 A*	*4500-CN^- C*			
	Spectrophotometric, Amenable		**D2036-98 B, -06 B**	**4500-CN^- G**	**4500-CN^- G**	**4500-CN^- G-99**	
	Spectrophotometric Manual		*D2036-98 A, -06 A*	*4500-CN^- E*	*4500-CN^- E*	*4500-CN^- E-99*	*USGS I-3300-85*
	Spectrophotometric Semi-automated	*335.4 (Rev. 1.0)*					
	Selective Electrode			4500-CN^- F	4500-CN^- F	4500-CN^- F-99	
	UV, Distillation, Spectrophotometric						Kelada-01 (Rev. 1.2; EPA 821-B-01-009)
	Micro Distillation, Flow Injection, Spectrophotometric						*QuikChem 10-204-00-1-X (Rev. 2.1)*
	Ligand Exchange and Amperometry		**D6888-04**				**OIA-1677, DW (EPA 821-R-04-001)**
	Headspace Gas Chromatography/Mass Spectrometry						**ME355.01 (Rev. 1.0)**

TOTAL **FREE** BOTH

Note: The Headspace GC/MS Method ME 355.01, Rev. 1.0 was approved through an expedited methods approval action for the determination of free cyanide in Aug. 2009 (74 FR 38348).

Separating the free and total methods results in the following modified Tables. Please note the following for both Tables:

1. For the Cyanide methods referenced from Standard Methods, 4500-CN- Sections A. Introduction and B. Preliminary Treatment of Samples are included by reference.
2. SM 4500-CN- C in the unapproved editions allowed the use of magnesium chloride (MgCl2) to be optional, provided no supportive data in changing the chemistry, and thus were not approved.

Modified Table for Total Cyanide

Methodology	EPA	ASTM	SM (ed.)	Other
Manual Distillation followed by Manual Spectrophotometry		*D2036-98 A, -06 A*	*4500-CN^- C* (18th, 19th & 20th) + *4500-CN^- E* (18th, 19th, 20th, 21st, 22nd, &-99 online)	*USGS I-3300-85*
Manual Distillation followed by Semi-Automated Spectrophotometry	*335.4 (Rev. 1.0)*			
Manual Distillation followed by Cyanide-Selective Electrode			*4500-CN^- C* (18th, 19th & 20th) + 4500-CN^- F (18th, 19th, 20th, 21st, 22nd, &-99 online)	
Automated UV Distillation followed by Automated Spectrophotometry				Kelada-01 (Rev. 1.2; EPA 821-B-01-009)
Micro Distillation, Flow Injection, followed by Automated Spectrophotometry				*QuikChem 10-204-00-1-X (Rev. 2.1)*

Modified Table for Free Cyanide

Methodology	EPA	ASTM	SM (ed.)	Other
~~*Manual Distillation followed by*~~ **Manual Spectrometry, Cyanides Amenable to Chlorination**[1, 2]		*D2036-98 A, -06 A* + **D2036-98 B, -06 B**	**4500-CN^- G** (18th, 19th, 20th, 21st, 22nd, &-99 online) + *4500-CN^- C* (18th, 19th & 20th) + *4500-CN^- E* (18th, 19th, 20th, 21st, 22nd, &-99 online)	
~~*Manual Distillation followed by*~~ Cyanide-Selective Electrode[2]			4500-CN^- F (18th, 19th, 20th, 21st, 22nd, &-99 online)	
~~Automated UV Distillation followed by~~ Automated Spectrophotometry[3]				Kelada-01 (Rev. 1.2; EPA 821-B-01-009)
~~**Ligand Exchange and**~~ **Amperometry**[2]		**D6888-04**		**OIA-1677, DW (EPA 821-R-04-001)**
Headspace Gas Chromatography/Mass Spectrometry				**ME355.01 (Rev. 1.0)**

[1] To determine cyanides amenable to chlorination, distillation as described in Part C of the Standard Method is still required. This requires analysis of two sample aliquots. The first aliquot is subjected to a chlorine treatment to decompose the cyanides. The second aliquot has no chlorine treatment. Both aliquots are distilled followed by manual spectrometry. The difference between the cyanide concentrations found in the two samples is expressed as cyanides amenable to chlorination.

[2] Free cyanide omits the distillation, digestion or ligand exchange.

[3] Measures "free" cyanides when UV-digestor is bypassed.

Clean versions of the modified Tables for Total and Free Cyanide are shown below.

Modified Table for Total Cyanide (clean version)

Methodology	EPA	ASTM	SM (ed.)	Other
Manual Distillation followed by Manual Spectrophotometry		D2036-98 A, -06 A	4500-CN^- C (18th, 19th & 20th) + 4500-CN^- E (18th, 19th, 20th, 21st, 22nd, &-99 online)	USGS I-3300-85
Manual Distillation followed by Semi-Automated Spectrophotometry	335.4 (Rev. 1.0)			
Manual Distillation followed by Cyanide-Selective Electrode			4500-CN^- C (18th, 19th & 20th) + 4500-CN^- F (18th, 19th, 20th, 21st, 22nd, &-99 online)	
Automated UV Distillation followed by Automated Spectrophotometry				Kelada-01 (Rev. 1.2; EPA 821-B-01-009)
Micro Distillation, Flow Injection, followed by Automated Spectrophotometry				QuikChem 10-204-00-1-X (Rev. 2.1)

Modified Table for Free Cyanide (clean version)

Methodology	EPA	ASTM	SM (ed.)	Other
Manual Spectrometry, Cyanides Amenable to Chlorination[1, 2]		D2036-98 A, -06 A + D2036-98 B, -06 B	4500-CN^- G (18th, 19th, 20th, 21st, 22nd, &-99 online) + 4500-CN^- C (18th, 19th & 20th) + 4500-CN^- E (18th, 19th, 20th, 21st, 22nd, &-99 online)	
Cyanide-Selective Electrode[2]			4500-CN^- F (18th, 19th, 20th, 21st, 22nd, &-99 online)	
Automated Spectrophotometry[3]				Kelada-01 (Rev. 1.2; EPA 821-B-01-009)
Amperometry[2]		D6888-04		OIA-1677, DW (EPA 821-R-04-001)
Headspace Gas Chromatography/Mass Spectrometry				ME355.01 (Rev. 1.0)

[1] To determine cyanides amenable to chlorination distillation as described in Part C of the Standard Method is still required. This requires analysis of two sample aliquots. The first aliquot is subjected to a chlorine treatment to decompose the cyanides. The second aliquot has no chlorine treatment. Both aliquots are distilled followed by manual spectrometry. The difference between the cyanide concentrations found in the two samples is expressed as cyanides amenable to chlorination.

[2] Free cyanide omits the distillation, digestion or ligand exchange.

[3] Measures “free” cyanides when UV-digestor is bypassed.