

**APPENDIX E**  
**DISINFECTANT RESIDUALS, DISINFECTION BYPRODUCTS AND**  
**DISINFECTION BYPRODUCT PRECURSORS**

**1101-E ANALYTICAL REQUIREMENTS**

A. General

1. Systems must use only the analytical method(s) specified in Part 1100 and Appendix E, or otherwise approved by EPA in the Federal Register, to demonstrate compliance with the requirements under Part 1100 or Appendix E. These methods are effective for compliance monitoring February 16, 1999, unless a different date is specified in this section or by this Director.
  
2. The following documents are incorporated by reference. Copies may be inspected at EPA's Drinking Water Docket, 1301 Constitutional Avenue, NW, EPA West, Room B102, Washington, DC, 20460, or at the National Archives and Records Administration (NARA). For information on the availability of this material at NARA, call 202-741-6030, or go to:  
[http://www.archives.gov/federal\\_register/code\\_or\\_federal\\_regulations/ibr\\_locations.htm](http://www.archives.gov/federal_register/code_or_federal_regulations/ibr_locations.htm)  
1. EPA Method 552.1 is in Methods for the Determination of Organic Compounds in Drinking Water-Supplement II, USEPA, August 1992, EPA/600/R-92/129 (available through National Information Technical Service (NTIS), PB92-207703). EPA Methods 502.2, 524.2, 551.1, and 552.2 are in Methods for the Determination of Organic Compounds in Drinking Water-Supplement III, USEPA, August 1995, EPA/600/R-95/131 (available through NTIS, PB95-261616). EPA Method 300.0 is in Methods for Determination of Inorganic Substances in Environmental Samples, USEPA, August 1993, EPA/600/R-93/100 (available through NTIS, PB94-121811). EPA Methods 300.1 and 321.8 are in Methods for the Determination of Organic and Inorganic Compounds in Drinking Water, Volume 1, USEPA, August 2000, EPA 815-R-00-014 (Available through NTIS, PB2000-106981). EPA Method 317.0, Revision 2.0, "Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis," USEPA, July 2001, EPA 815-B-01-001, EPA Method 326.0, Revision 1.0, "Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis," USEPA, June 2002, EPA 815-R-03-007, EPA Method 327.0, Revision 1.1, "Determination of Chlorite Ion in Drinking Water Using Lissamine Green B and Horseradish Peroxidase with Detection by Visible Spectrophotometry," USEPA, May 2005, EPA 815-R-05-008 and EPA Method 552.3, Revision 1.0, "Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection," USEPA, July 2003, EPA-815-B-03-002 can be accessed and downloaded directly on-line at <http://www.epa.gov/safewater/methods/sourcalt.html>. EPA Method 415.3, Revision 1.1, "Determination of Total Organic Carbon and Specific UV Absorbance at 254nm in Source Water and Drinking Water," USEPA, February 2005, EPA/600/R-05/055 can be accessed and downloaded directly online at [www.epa.gov/nerlcwww/ordmeth.htm](http://www.epa.gov/nerlcwww/ordmeth.htm). Standard Methods 4500-C1 D, 4500-C1 E, 4500-C1 F, 4500-C1 G, 4500-C1 H, 4500-C1 I, 4500-C1 O<sub>2</sub> D, 4500-C1 O<sub>2</sub> E, 6251 B, and 5910 B shall be followed in accordance with Standard Methods for the Examination of Water and Wastewater, 19<sup>th</sup> or 20<sup>th</sup> Editions, American Public Health Association, 1995 and 1998, respectively. The cited methods published in either edition may be used. Standard Methods shall be followed in accordance with the Supplement to the 19<sup>th</sup> Edition of Standard methods for the Examination of Water and Wastewater, or the Standard Methods for the Examination of Water and Wastewater, 20<sup>th</sup> Edition, American Public Health Association, 1996 and 1998, respectively. The cited methods published in either edition may be used. Copies may be obtained from the American Public Health Association, 1015 Fifteenth Street, NW, Washington, DC, 20005. Standard Methods 4500-C1 D-00, 4500-C1 E-00, 4500-C1 F-00, 4500-C1 G-00, 4500-C1 H-00, 4500-C1 I-00, 4500-C1 O<sub>2</sub> E-00, 6251 B-94, 5310 B-00, 5310 C-00, and 5310 D-00, and 5910 B-00 are available at <http://www.standardmethods.org> or at EPA's Water Docket. 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 are IBR-approved. ASTM Methods D 1253-86 and D1253-86 (Reapproved 1996) shall be followed in accordance with the Annual Book of ASTM Standards, Volume 11.01, American Society for Testing and Materials International, 1996 or any ASTM edition containing the IBR-approved version of the method may be used. ASTM Standards, Volume 11.01, American Society for Testing and Materials International, 2004 or any ASTM edition containing the IBR-approved version of the method may be used. ASTM Method D 6581-00 shall be followed in accordance with the Annual Book Of ASTM Standards, Volume 11.01, American Society for Testing and Materials International, 2001 or any ASTM edition containing the IBR-approved version of the method may be used;

B. Disinfection byproducts

1. Systems must measure disinfection byproducts by the methods (as modified by the footnotes) listed in the following table or one of the alternative methods listed in Appendix A to subpart C of 40 C.F.R. pt. 141:

**Table 1101-E-1 Approved Methods for Disinfection Byproduct Compliance Monitoring**

Contaminant and methodology <sup>1</sup>	EPA method	Standard method <sup>2</sup>	SM Online <sup>3</sup>	ASTM method <sup>4</sup>
<b>TTHM</b>				
P&T/GC/EICD & PID	502.2 <sup>5</sup>	.....	.....	
P&T/GC/MS	524.2	.....	.....	
LLE/GC/ECD	551.1	.....	.....	
<b>HAA5</b>				
LLE(diamethane)/GC/ECD	.....	6251 B <sup>6</sup>	6251 B-94	
SPE(acidic methanol)/GC/ECD	552.1 <sup>6</sup>	.....	.....	
LLE(acidic methanol)/GC/ECD	552.2, 552.3	.....	.....	
<b>Bromate</b>				
Ion chromatography	300.1	.....	.....	D 6581-00
Ion chromatography & post column reaction	317.0 Rev 2.0 <sup>7</sup> , 326.0 <sup>7</sup>	.....	.....	
IC/ICP-MS	321.8 <sup>7,8</sup>	.....	.....	
<b>Chlorite</b>				
Amperometric titration	.....	4500-ClO <sub>2</sub> E <sup>9</sup>	4500-ClO <sub>2</sub> E-00 <sup>9</sup>	
Spectrophotometry	327.0 Rev 1.1 <sup>9</sup>	.....	.....	
Ion chromatography	300.0, 300.1, 317.0, Rev 2.0, 326.0	.....	.....	D 6581-00

<sup>1</sup> P&T = purge and trap; GC = gas chromatography; EICD = electrolytic conductivity detector; PID = photoionization detector; MS = mass spectrometer; LLE = liquid/liquid extraction; ECD = electron capture detector; SPE = solid phase extraction; ICP-MS = inductively coupled plasma/mass spectrometer.

<sup>2</sup> 19<sup>th</sup> and 20<sup>th</sup> editions of Standard Methods for the Examination of Water and Wastewater, 1995 and 1998, respectively, American Public Health Association; either of these editions may be used.

<sup>3</sup> The Standard Methods Online version that is approved is indicated by the last two digits in the method number which is the year of approval by the Standard Method Committee. Standard Methods Online are available at <http://www.standardmethods.org>.

<sup>4</sup> Annual Book of ASTM Standards, 2001 or any year containing the cited version of the method, Vol 11.01.

<sup>5</sup> If TTHMs are the only analytes being measured in the sample, then a PID is not required.

<sup>6</sup> The samples must be extracted within 14 days of sample collection.

<sup>7</sup> Ion chromatography & post column reaction or IC/ICP-MS must be used for monitoring of bromate for purposes of demonstrating eligibility or reduced monitoring, as prescribed in § 1103(B)(3)(b).

<sup>8</sup> Samples must be preserved at the time of sampling with 50 mg ethylenediamine (EDA)/L of sample and must be analyzed within 28 days.

<sup>9</sup> Amperometric titration or spectrophotometry may be used for routine daily monitoring of chlorite at the entrance to the distribution system, as prescribed in §1103(B)(2)(a)(1). Ion chromatography must be used for routine monthly monitoring of chlorite and additional monitoring of chlorite in the

distribution system, as prescribed in §1103(B)(2)(a)(2) and (B)(2)(b).

2. Analyses under this section for disinfection byproducts must be conducted by laboratories that have received certification by EPA or the Director, except as specified under paragraph(D)(3)of this section. To receive certification to conduct analyses for the DBP contaminants in §§ 207, and NNPDWR Parts XXII and XXIII or this part, the laboratory must:

- a. Analyze Performance Evaluation (PE) samples that are acceptable to EPA at least once during each consecutive 12 month period by each method for which the laboratory desires certification.
- b. Until March 31, 2007, in these analyses of PE samples, the laboratory must achieve quantitative results within the acceptance limit on a minimum of 80% of the analytes included in each PE sample. The acceptance limit is defined as the 95% confidence interval calculated around the mean of the PE study between a maximum and minimum acceptance limit of +/-50% and +/-15% of the study mean.
- c. Beginning April 1, 2007, the laboratory must achieve quantitative results on the PE sample analyses that are within the following acceptance limits:

**Table 1101-E-2 - Acceptance limits for Disinfection Byproducts**

DBP	Acceptance limits (percent of true value)	Comments
TTHM		
Chloroform	±20	Laboratory must meet all 4 individual THM acceptance limits in order to successfully pass a PE sample for TTHM.
Bromodichloromethane	±20	
Dibromochloromethane	±20	
Bromoform	±20	
HAA5		
Monochloroacetic Acid	±40	Laboratory must meet the acceptance limits for 4 out of 5 of the HAA5 compounds in order to successfully pass a PE sample of HAA5.
Dichloroacetic Acid	±40	
Trichloroacetic Acid	±40	
Monobromoacetic Acid	±40	
Dibromoacetic Acid	±40	
Chlorite	±30	
Bromate	±30	

- d. Beginning April 1, 2007, report quantitative data for concentrations at least as low as the ones listed in the following table for all DBP samples analyzed for compliance with §§ 208, and NNPDWR Parts XXII and XXIII of this part:

**Table 1103-E-3 Minimum Reporting Level for Disinfection Byproducts**

DBP	Minimum reporting level (mg/L) <sup>1</sup>	Comments
TTHM <sup>2</sup>		

Chloroform	0.0010	
Bromodichloromethane	0.0010	
Dibromochloromethane	0.0010	
Bromoform	0.0010	
HAA5 <sup>2</sup>		
Monochloroacetic Acid	0.0020	
Dichloroacetic Acid	0.0010	
Trichloroacetic Acid	0.0010	
Monobromoacetic Acid	0.0010	
Dibromoacetic Acid	0.0010	
Chlorite	0.020	Applicable to monitoring as prescribed in §1103 (B)(2)(a)(ii) and (B)(2)(b)
Bromate	0.0050 or 0.0010	Laboratories that use EPA Methods 317.0 Revision 2.0, 326.0, or 312.8 must meet a 0.0010mg/L MRL for bromate

<sup>1</sup> The calibration curve must encompass the regulatory minimum reporting level (MRL) concentrations lower than the regulatory MRL as long as the precision and accuracy criteria are met by analyzing an MRL check standard at the lowest reporting limit chosen by the laboratory. The laboratory must verify the accuracy of the calibration curve at the MRL concentration by analyzing an MRL check standard with a concentration less than or equal to 110% of the MRL with each batch of samples. The measured concentration for the MRL check standard must be ±50% of the expected value, if any field sample in the batch has a concentration less than 5 times the regulatory MRL. Method requirements to analyze higher concentration check standards and meet tighter acceptance criteria for them must be met in addition to the MRL check standard requirement.

<sup>2</sup> When adding the individual trihalomethane or haloacetic acid concentration to calculate the TTHM or HAA5 concentrations, respectively, a zero is used for any analytical results that is less than the MRL concentration for that DBP, unless otherwise specified by the Director.

3. A party approved by EPA or NNEPA must measure daily chlorite samples at the entrance to the distribution system.

C. Disinfectant residuals.

1. Systems must measure residual disinfectant concentrations for free chlorine, combined chlorine (chloramines), and chlorine dioxide by the methods listed in the following table or one of the alternative methods listed in Appendix A to subpart C of 40 C.F.R. pt. 141:

**Table 1101-E-4 Approved Methods for Disinfectant Residual Compliance Monitoring**

Methodology	Standard Method (19 <sup>th</sup> or 20 <sup>th</sup> ED)	SM Online <sup>1</sup>	ASTM method	EPA method	Residual Measured <sup>2</sup>			
					Free Chlorine	Combined Chlorine	Total Chlorine	Chlorine dioxide
Amperometric Titration	4500-C D	4500-C D-00	D 1253-86 (96), 03		X	X	X	
Low Level Amperometric Titration	4500-C E	4500-C E-00					X	
DPD Ferrous Titrimetric	4500-C F	4500-C F-00			X	X	X	

DPD Colorimetric	4500-C G	4500-C G-00			X	X	X	
Syringaldazine (FACTS)	4500-C H	4500-C H-00			X			
Iodometric Electrode	4500-C I	4500-C I-00					X	
DPD	4500-C O <sub>2</sub> D							X
Amperometric Method II	4500 C O <sub>2</sub> E	4500-C O <sub>2</sub> E-00						X
Lissamine Green Spectrophotometric.				327.0 Rev				X

<sup>1</sup> The standard Methods Online version that is approved is indicated by the last two digits in the method number which is the year of approval by the Standard Method Committee. Standard Methods Online are available at <http://www.standardmethods.org>.

<sup>2</sup> X indicates method is approved for measuring specified disinfectant residual. Free chlorine or total chlorine may be measured for demonstrating compliance with the chlorine MRDL and combined chlorine, or total chlorine may be measured for demonstrating compliance with the chloramine MRDL.

2. If approved by the NNEPA, systems may also measure residual disinfectant concentrations for chlorine, chloramines, and chlorine dioxide by using DPD colorimetric test kits.
3. A party approved by EPA or NNEPA must measure residual disinfectant concentration.

D. Additional analytical methods. Systems required to analyze parameters not included in paragraphs (B) and (C) of this section must use the following methods or one of the alternative methods listed in Appendix A to subpart C of 40 C.F.R. pt. 141. A party approved by EPA or NNEPA must measure these parameters.

1. Alkalinity. All methods allowed in Appendix C § 701-C (A) for measuring alkalinity.
2. Bromide. EPA Method 300.0, 300.1, 317.0 Revision 2.0, 326.0, or ASTM D 6581-00.
3. Total Organic Carbon (TOC). Standard Method 5310 B or 5310 B-00 (High-Temperature Combustion Method) or Standard Method 5310 C or 5210 C-00 (Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method) or Standard Method 5310 D or 5310 D-00 (Wet-Oxidation Method) or EPA Method 415.3 Revision 1.1. Inorganic carbon must be removed from the samples prior to analyses. TOC samples may not be filtered prior to analysis. TOC samples must be acidified at the time of sample collection to achieve pH less than or equal to 2 with minimal addition of the acid specified in the method or by the instrument manufacturer. Acidified TOC samples must be analyzed within 28 days.
4. Specific Ultraviolet Absorbance (SUVA). SUVA is equal to the UV absorption at 254nm (UV<sub>254</sub>) (measured in m<sup>-1</sup> divided by the dissolved organic carbon (DOC) concentration (measured as mg/L). In order to determine SUVA, it is necessary to separately measure UV<sub>254</sub> and DOC. When determining SUVA, systems must use the methods stipulated in paragraph (D)(4)(i) of this section to measure DOC and the method stipulated in paragraph (D)(4)(ii) of this section to measure (UV<sub>254</sub>). SUVA must be determined on water prior to the addition of disinfectants/oxidants by the system. DOC and (UV<sub>254</sub>) samples used to determine a SUVA value must be taken at the same time and at the same location.
  - a. Dissolved Organic Carbon (DOC). Standard Method 5310 B or 5310 B-00 (High-Temperature Combustion Method) or Standard Method 5310 C or 5310 C-00 (Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method) or Standard Method 5310 D or 5310 D-00 (Wet-Oxidation Method) or EPA method 415.3 Revision 1.1. DOC samples must be filtered through the 0.45 µm pore diameter filter as soon as practical after sampling, not to exceed 48 hours. After filtration, DOC samples must be acidified to achieve pH less than or equal to 2 with minimal addition of the acid specified in the method or by the instrument manufacturer. Acidified DOC samples must be analyzed within 28 days of sample collection. Inorganic carbon must be removed from the samples

prior to analysis. Water passed through the filter prior to filtration of the sample must serve as the filtered blank. This filtered blank must be analyzed using procedures identical to those used for analysis of the samples and must meet the following criteria: DOC <0.5mg/L.

- b. Ultraviolet Absorption at 254 nm (UV<sub>254</sub>). Method 5910 B or 5910 B-00 (Ultraviolet Absorption Method) or EPA Method 415.3 Revision 1.1. UV absorption must be measured at 253.7 nm (may be rounded off to 254 nm). Prior to analysis, UV<sub>254</sub> samples must be filtered through a 0.45 µm pore-diameter filter. The pH of UV<sub>254</sub> samples may not be adjusted. Samples must be analyzed as soon as practical after sampling, not to exceed 48 hours.
5. pH. All methods allowed in Appendix A § 403-A (A) for measuring pH.
  6. Magnesium. All methods allowed in Appendix A-403-A (A)(1.)