

**STATUS REPORT ON ANALYTICAL METHODS  
TO SUPPORT THE DISINFECTANT/DISINFECTION  
BY-PRODUCTS REGULATION**

August 1992

**Background**

The United States Environmental Protection Agency (EPA) is developing national regulations to control disinfectants and disinfection by-products (D/DBPs) in public drinking water supplies. Twelve D/DBPs have been identified for possible regulation under this rule<sup>123</sup>, based on available occurrence, exposure, and health effects data. EPA intends to set maximum contaminant levels (MCLs) for these D/DBPs, and analytical methods will be specified for use in demonstrating compliance with each MCL. This document provides a summary of the analytical methods that EPA intends to propose as compliance monitoring methods. A discussion of surrogate measurements that are being considered for inclusion in the regulation is also provided.

There are several technical issues that EPA is trying to resolve before the methods discussed in this document are proposed/promulgated. The public is encouraged to contact EPA, if they have information that will help EPA in this process. Information should be addressed to:

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**Disinfectants:**

**Chlorine and Chloramines.** The measurement of chlorine residuals will be required as part of the D/DBP Rule in order to demonstrate compliance with MCLs for chlorine and monochloramine. The utility will have the option of either measuring free or total chlorine residuals for the chlorine MCL. Compliance with the monochloramine MCL will be based on a total chlorine residual measurement, because monochloramine cannot be practically measured by itself.

There are many analytical methods available for measuring chlorine residuals, and each has certain limitations. All methods are subject to interferences, so the accuracy and

precision of the analysis will vary with matrix. Low level free chlorine measurements are subject to interference errors from chloramines and other oxidants.

Several methods for measuring chlorine residuals were promulgated with the Surface Water Treatment Rule (SWTR)<sup>4</sup>: 1) amperometric titration; 2) DPD ferrous titrimetric method; 3) DPD colorimetric method; and 4) the leuco crystal violet (LCV) method. These were referenced to the 16th Edition of *Standard Methods for the Examination of Water and Wastewater*<sup>5</sup>. EPA used these methods as the starting point for determining methods that are applicable to the D/DBP Rule. Methods listed in the 17th Edition of *Standard Methods*<sup>6</sup> were also considered. Table 1 summarizes the methods most likely to be proposed with the D/DBP Rule. The methods required to demonstrate compliance with the SWTR will also be updated to be consistent with the D/DBP Rule.

EPA intends to propose three of the four chlorine residual methods from the SWTR, when the D/DBP Rule is proposed. The LCV method will not be proposed. It was not included in the 17th Edition of *Standard Methods*, due to its relative difficulty and lack of comparative advantages. EPA thinks it is unlikely that this method is being used, so dropping it should have little effect on the regulated community.

EPA is considering approval of two additional methods for compliance monitoring: 1) the syringaldazine (FACTS) method for free chlorine and 2) the iodometric electrode method for total chlorine. Both methods are included in the 17th Edition of *Standard Methods*.

Method 4500-Cl E for measuring low levels of total chlorine residual is also available in the 17th Edition of *Standard Methods*. Although it is not useful for measuring total chlorine residuals at concentrations near the MCL, it is useful for determining compliance with the SWTR requirements for a detectable residual in the distribution system. Therefore, EPA is considering approval of this method when it updates methods for the SWTR. Data obtained using this method can also be used to demonstrate compliance with the total chlorine residual MCL in the D/DBP Rule.

The 18th Edition of *Standard Methods*<sup>7</sup> will be available for purchase in August, 1992, so the D/DBP Rule will cite it for descriptions of the chlorine residuals methods. The method numbers did not change from the 17th to the 18th edition, so the numbers given in Table 1 can be used with either edition. Since EPA is required to review its regulations every 3 years, EPA anticipates incorporating the latest versions of the methods into the D/DBP Rule each time it is reviewed.

Historically, EPA has required all analyses that are done to demonstrate compliance with an MCL, be performed by a certified laboratory. Because chlorine residuals are not stable, these samples must be analyzed immediately and cannot be transported to an off-site laboratory. Utility personnel have been performing chlorine residual analyses either in the field or in the treatment plant. EPA feels these measurements should continue to be made at the water system by any person acceptable to the State. It is not EPA's intent to require the certification of each water system for chlorine residual measurements.

EPA will continue to allow the use of DPD colorimetric test kits for field measurements of chlorine residuals, if they are approved by the State.

**Chlorine Dioxide.** The SWTR promulgated two methods for measuring chlorine dioxide residuals: 1) amperometric titration and 2) the DPD method. The 16th Edition of *Standard Methods* was cited as the reference. As discussed above for chlorine residual measurements, the latest versions of methods for measuring chlorine dioxide residuals (see Table 1) will be cited in the D/DBP Rule.

The 17th Edition of *Standard Methods* proposes a second amperometric titration method (4500-ClO<sub>2</sub> E) for measuring chlorine dioxide residuals. EPA is considering adding it as an acceptable compliance monitoring method.

The methods for chlorine dioxide residuals are indirect methods, because the concentrations are determined by difference. Amperometric titration methods are preferred over the DPD method, if they are used by highly trained personnel.

It is EPA's intent to continue to allow the measurement of chlorine dioxide residuals at the water system by any person acceptable to the State.

Due to the limitations of the current methodology, EPA is seeking information on new methodology that may be applicable for compliance monitoring. New methods must provide demonstrated advantages over the current methods and have the potential for being distributed in a standard format to interested public in the timeframe of the D/DBP regulation. New methods must be useable in the field or by utility personnel.

### **Disinfection By-Products:**

**Trihalomethanes.** There are two methods currently approved for THM compliance monitoring: EPA Methods 501.1 and 501.2. These packed column, gas chromatography (GC) methods were

promulgated with the 1979 THM Rule<sup>4</sup>. EPA intends to propose two capillary column GC methods by the end of 1992: EPA Methods 502.2<sup>9</sup> and 524.2<sup>10</sup>. After a 45 day comment period, the methods will be promulgated, and they can be used for THM compliance monitoring effective 30 days after promulgation. EPA Methods 502.2 and 524.2 are in general use in many laboratories, because they are used to measure the concentrations of volatile organic compounds (VOCs) in drinking water.

EPA Methods 502.1 and 524.1<sup>9</sup> are not being proposed in 1992 and they are not being considered for the D/DBP Rule, because they use packed column chromatography. The GC technology has progressed to the point that packed columns are becoming obsolete. EPA is considering eliminating packed column GC methods (EPA Methods 501.1 and 501.2) from the list of approved THM compliance monitoring methods when the D/DBP Rule is proposed. This would not be implemented until the monitoring requirements of the D/DBP Rule become effective.

EPA Method 551<sup>11</sup> is the only new method that is likely to be added for THM compliance monitoring when the D/DBP Rule is promulgated. It involves adjusting the ionic strength of the sample, extracting the analytes into methyl-tertiary-butyl ether (MTBE), and analyzing the extract by capillary column GC with electron capture detection (ECD). This method can also be used to measure the concentrations of haloacetonitriles, chloropicrin, 1,1-dichloropropanone, 1,1,1-trichloropropanone, and chloral hydrate, if the appropriate dechlorinating agents are used.

Several laboratories around the country have modified EPA Method 551 by using pentane, instead of MTBE, as the extraction solvent. When this is done, chloral hydrate (CH) is not included in the analysis, because CH is too polar to be extracted by pentane. EPA Method 551 permits the analyst to modify GC columns, GC conditions, detectors, extraction techniques, concentration techniques, internal standard or surrogate compounds, as long as the analyst demonstrates the modified method still meets the performance criteria established in the method. Therefore, if Method 551 is approved for THM compliance monitoring, approval to use pentane will not be considered necessary as long as the method performance criteria are met. This will eliminate some of the need for approval of alternative test procedures (ATPs).

Many commercial sources of MTBE are contaminated with chloroform, necessitating cleanup prior to use in THM analyses. MTBE can be purified by distillation using appropriate safety precautions, but it should not be stored for long periods of time, in order to prevent the formation of peroxides. At least some lots of OmniSolv (EMScience) MTBE labeled "Suitable for Spectrophotometry, Liquid Chromatography, Gas Chromatography,

Residue Analysis, Assay by GC: 99.9% pure" have not contained measurable levels of chloroform or chlorinated solvents, indicating suitable purity MTBE can be produced commercially. This should encourage laboratories to make the need for high purity MTBE known to their local solvent suppliers. Manufacturers may be willing to prepare and market special lots, when they are aware of a market for their product.

The EPA methods that are likely to be approved for compliance monitoring of THMs are summarized in Table 2. All of these methods include the option to use ascorbic acid as a dechlorinating agent. This practice is under review, because ascorbic acid may cause the loss of brominated THMs under some conditions. If laboratories are aware of alternatives to the HCl and ascorbic acid required by EPA Method 524, they are encouraged to share that information with EPA. (Sodium thiosulfate and HCl were originally included in 524, but they cause interference problems with some of the early eluting analytes included in the method. Thiosulfate and HCl can still be used, if the sample does not have to be analyzed for the early eluting compounds.)

**Chloral Hydrate.** EPA Method 551<sup>11</sup> will be proposed as the compliance monitoring method for chloral hydrate (CH), but additional work must be done before the method is ready for general use. Chloral hydrate is subject to base-catalyzed hydrolysis, and the current version of the method does not provide a mechanism for preventing hydrolysis. This method will require the addition of a preservative, probably in the form of acidification. Work is underway to evaluate preservatives for CH. EPA solicits data demonstrating the stability of CH in drinking water samples. The data must indicate the dechlorinating agent used, preservation procedure, sample pH, storage conditions and holding time.

The regular dechlorinating agent ( $\text{NH}_4\text{Cl}$ ) recommended in Method 551 cannot be used in some drinking water matrices, because it interferes with the CH analysis. Either ascorbic acid or sodium sulfite can be used under those circumstances. Since ascorbic acid causes problems with THM analyses in some matrices, EPA prefers the use of sodium sulfite. As part of the effort to evaluate preservation techniques for CH, EPA will look at how THMs are affected. It is anticipated that a technique can be developed in which THMs and CH could be measured in the same sample using EPA Method 551. If successful, this would reduce the monitoring costs associated with these analytes.

Some laboratories have expressed concern about the safety of using MTBE. EPA recommends that ether extracts should be stored in an explosion-proof refrigerator/freezer.

The availability of standards for CH has been a problem for laboratories. However, dilute solutions of CH in acetone are now available from NSI Environmental Solutions, Inc. (Research Triangle Park, NC) [Catalogue # 001179-01-01, \$32.00] This is an EPA certified standard. A neat standard is available from Supelco (Bellefonte, PA) [Catalogue # 4-8048]. Other commercial sources may become available during the next year.

Very few laboratories are doing CH analyses. EPA is not aware of any commercial laboratories, but this should change over the next few years as utilities include it as a by-product of interest in their bench and pilot scale treatment studies.

Chloral hydrate will be included in the EPA Performance Evaluation (PE) Studies by the end of 1992. This will provide laboratories an opportunity to evaluate how well the method is performing for them. It will also provide EPA with an estimate of how many laboratories are doing CH analyses and how well they are doing.

**Haloacetic Acids.** The EPA method that will be proposed for haloacetic acid (HAA) compliance monitoring will give the analyst several options. The initial (standard) version of Method 552<sup>11</sup> specified the following steps in the procedure: 1) extraction with MTBE after sample pH adjustment to >11.5; 2) discard MTBE fraction and adjust pH of sample to <0.5; 3) extraction with MTBE; 4) concentration and drying of the extract; 5) conversion of the HAAs to their methyl esters using diazomethane; and 6) analysis by capillary column GC/ECD.

A microextraction option was later added to EPA Method 552<sup>12</sup>. This option eliminated the cleanup extraction, extract concentration, and extract drying steps. The 18th Edition of *Standard Methods* will include a microextraction method for measuring HAAs. EPA is considering it as a compliance monitoring method, because it is equivalent to the option described in Method 552.

EPA is also developing a liquid/solid extraction technique using ion exchange resins and an acidic methanol derivatization procedure<sup>13</sup>. A written procedure should be available for public distribution by the end of 1992, and it will be designated EPA Method 552.1<sup>10</sup>.

All of the above procedures will be proposed as compliance monitoring techniques; all will be covered under EPA Method 552. Giving the analyst the flexibility to choose extraction technique and derivatization method should make it easier to begin this analysis in the laboratory. The acidic methanol derivatization procedure will also eliminate the concern expressed by some states and other entities over the use of diazomethane due to

safety issues.

The quantitation procedures specified in the current version of EPA Method 552<sup>11</sup> must be clarified prior to proposal of the D/DBP Rule. The initial procedure (described above in the first paragraph under HAAs) does not require that standards be extracted, and no correction is made for analytes which are not fully extracted from the aqueous sample (e.g., dibromoacetic acid [DBAA]). The microextraction option recommends the preparation of aqueous standards that are carried through the same procedure as the samples. Using this option, the analytical results are automatically corrected for less than 100% extraction efficiencies. Either calibration method will be acceptable for compliance monitoring, if EPA only sets MCLs for dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), because both acids are extracted from water at > 90% efficiency. However, EPA is also considering a total HAA (THAA) MCL. Samples from utilities with high levels of bromide ion in their source water may contain high levels of the brominated and mixed bromochloro-acetic acids. Since these acids are not extracted from water as efficiently as the chlorinated acids, use of the initial HAA analytical procedure (described above in the first paragraph under HAAs) would give a lower THAA result than the microextraction procedure. For this reason, future versions of Method 552 will specify that aqueous standards be used for calibration purposes. Analyses performed to meet compliance monitoring requirements for a THAA MCL must use aqueous standards for calibration purposes.

Five of the HAAs (monochloroacetic acid [MCAA], DCAA, TCAA, monobromoacetic acid [MBAA], and DBAA) have been included in EPA PE studies, since study WS026 (spring, 1990). A calibration procedure for the HAAs was not specified with the PE studies, so laboratories reported data from both procedures. Since the two procedures are not equivalent for several of the HAAs, EPA will specify that HAA PE samples be analyzed using aqueous standards in future PE studies.

EPA Method 552 specifies the HAA standards be prepared in MTBE, but many laboratories are using methanol instead of MTBE. Recent work by Yuefeng Xie<sup>14</sup> at the University of Massachusetts, indicates that over time the acids will undergo conversion to their methyl ester analogs when stored in methanol. The conversion rate varies with analyte and storage conditions. Unless the analyst specifically checks for this conversion by analyzing a non-derivatized standard, it is unlikely the problem would be detected. The use of ester or mixed free acid and ester standards will provide inaccurate results, due to differences in extraction efficiencies between acids and esters. EPA has not studied this problem, but recommends that if laboratories must continue to use methanol, they monitor their methanol standards for this conversion, and prepare fresh standards when esters are

detected. As an alternative, laboratories should prepare HAA standards in MTBE.

There are 9 haloacetic acids (HAAs) that could potentially be included in a THAA MCL. However, the EPA Method 552 only includes 6 of the HAAs (MCAA, DCAA, TCAA, MBAA, DBAA, and bromochloroacetic acid [BCAA]). Tribromoacetic acid (TBAA) is not included, because it is not reliably measured using the current techniques. The remaining 2 HAAs (bromodichloroacetic acid [BDCAA] and dibromochloroacetic acid [DBCAA]) have not been tested with Method 552, because standards are not commercially available. It is unlikely that TBAA, BDCAA, or DBCAA will be included in Method 552 in the timeframe of this regulation.

EPA is aware of three suppliers that are selling or plan to sell HAA standards:

- 1) Supelco, Inc. (Bellefonte, PA) is distributing a calibration standard that contains MCAA, DCAA, TCAA, MBAA, DBAA, and BCAA (catalogue # 4-8047). They will also market a BCAA standard in solution form as a custom chemical.
- 2) Absolute Standards, Inc. (New Haven, CT) is selling a HAA QC sample, containing MCAA, DCAA, TCAA, MBAA, DBAA, 2,4-dichlorophenol (24DCPh), and 2,4,6-trichlorophenol (246TCPH). A standard containing the methyl derivatives of the same compounds is also available, thus, providing laboratories a mechanism for checking the derivatization efficiency of their method. BCAA will soon be added to the free acid standard mixture, and should be available for release in August, 1992 (catalogue # 30054).
- 3) ULTRA Scientific (North Kingstown, RI) plans to release a standard containing MCAA, DCAA, TCAA, MBAA, DBAA, BCAA, 24DCPh, and 246TCPH (catalogue # PHM-552A). The standard is tentatively scheduled for release in early August, 1992, assuming successful results from a 60 day time storage study.

EPA believes there will be adequate laboratory capability available by the time compliance monitoring for HAAs is required. Sixteen laboratories participated in the WS029 PE study by analyzing the HAA sample. This number is expected to increase significantly over the next few years, as laboratories expand their analyses to address the new regulations.

**Chlorite, (Chlorate) and Bromate.** An ion chromatography method will be proposed as the compliance monitoring method for these anions. EPA does not intend to propose an MCL for the chlorate ion ( $\text{ClO}_3^-$ ), but a description of the analytical method is presented here since it can be determined with the chlorite ion ( $\text{ClO}_2^-$ ). The current version of EPA Method 300.0 Part B<sup>15</sup> can be used for measuring  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  in drinking waters. In some cases, a weaker carbonate eluent may be required<sup>16</sup>, because  $\text{ClO}_2^-$

elutes in the void volume in high ionic strength samples. A change in the eluent strength is permitted as part of Method 300.0 Part B, as long as the analyst demonstrates that the quality control requirements outlined in the method are met (see Sections 10.1.1 and 11.1 of the method).

Chlorite ion is unstable in many waters<sup>17</sup>, so a preservation technique will be required if the samples cannot be analyzed within 15 minutes of collection. Recent studies<sup>16,18</sup> indicate ethylenediamine (EDA) is a suitable preservative for  $\text{ClO}_2^-$ , and it does not adversely affect analysis of the other anions at the concentrations typically found in drinking water. Therefore, EPA is considering requiring the addition of EDA to samples analyzed for  $\text{ClO}_2^-$  compliance monitoring.

Measurement of  $\text{ClO}_2^-$  in samples containing a free chlorine residual will also require the use of EDA. Free chlorine reacts with  $\text{ClO}_2^-$  to form  $\text{ClO}_3^-$  and chloride.

Samples containing a chlorine dioxide residual must be sparged with an inert gas (e.g., He or Ar) at the time of collection to eliminate the chlorine dioxide. Otherwise,  $\text{ClO}_2$  will continue to form  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  in the samples. Prior to sparging, the samples must be protected from light to prevent photodecomposition of the chlorine dioxide to form  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$ .<sup>19</sup>

EPA is aware of other techniques (e.g., flow injection analysis [FIA]) that are being used to measure chlorite and chlorate. FIA and/or any other applicable procedure will be considered as a potential compliance monitoring method, if it is demonstrated to be as accurate and precise as ion chromatography. The technique would have to be available in a standard format for public distribution.

Analyses for bromate ion in drinking water samples will require a modification to the EPA ion chromatography method, due to the interference from chloride present in these matrices. One approach is to pretreat the sample with a silver media in order to remove the chloride<sup>20</sup>. When this technique is used, traces of silver are deposited on the IC analytical column, necessitating the removal of silver before using the column for bromide analyses. Another alternative is to change the eluent. Recent studies<sup>16,18</sup> demonstrate that substituting a borate eluent for the carbonate eluent specified in the method not only provides the resolution required to quantitate bromate ion in drinking water, but also gives a more stable baseline. All the DBP anions can be measured using the same chromatographic conditions with the borate eluent. Sections 10.1.1 and 11.1 of EPA Method 300.0 Part B permit the use of the borate eluent as long as the analyst demonstrates that the quality control requirements outlined in

the method are met.

EPA is concerned about the ability to reliably measure bromate at the levels necessary for this regulation. Studies are underway in several laboratories, including EPA, to examine ways to lower the detection limit for this anion. Concentration techniques are the most promising avenues of research. EPA requests information on any techniques that are demonstrated to be effective in drinking water matrices.

Chlorite, chlorate and bromate ions are now included in EPA PE studies. Thirteen laboratories participated in study WS029.

#### Surrogate Measurements:

**Simulated Distribution System (SDS) Test.** EPA may consider the use of a Simulated Distribution System (SDS) test as a surrogate measurement of DBP concentrations in the distribution system. EPA will recommend a modified version of the procedure described in Method 5710 E in the 17th edition of *Standard Methods* (reference will be updated to the 18th edition when proposed). The method is written for use in determining THM concentrations, but it can be extended to other DBPs as long as appropriate dechlorinating agents are used after the storage period. Results of the test are not valid, if there is no detectable chlorine residual at the end of the storage period. If the test is used to determine a "worst case" for consumer exposure, then the sample storage period should be representative of the maximum distribution system temperature, pH, chlorine concentration and the longest detention time in the distribution system. EPA will accept data comparing results from the SDS test to actual distribution system samples. The data must include a full description of the SDS test conditions, including dechlorination procedures and analytical methods used to quantitate the DBPs. Information concerning the data from distribution system samples should include temperature, chlorine residuals, pH, and approximate detention time of the water in the system.

**Total Organic Carbon.** There are 3 methods for measuring organic carbon listed in the 17th Edition (18th Edition) of *Standard Methods*, and 2 of them are applicable to requirements of the D/DBP rule. The persulfate-ultraviolet oxidation method (5310 C) and the wet-oxidation method (5310 D) provide the sensitivity necessary for low level organic carbon measurements, so they will be recommended if organic carbon is proposed in the D/DBP rule as a surrogate measurement for DBP precursors. Depending upon the sample pretreatment, several different organic carbon fractions are measured by these methods. If the sample is filtered through a 0.45 $\mu$ m pore size filter before analysis, Dissolved Organic Carbon (DOC) is measured. Purging the sample

prior to analysis results in the measurement of Nonpurgeable Organic Carbon (NPOC). Both of these parameters have been used as indicators of raw water quality. EPA will accept information concerning the use of DOC or NPOC as a surrogate for DBP precursors in source water.

**Total Organic Halide.** Method 5320 B in the 17th Edition (18th Edition) of *Standard Methods* will be recommended for determining Total Organic Halide (TOX). The sample must be dechlorinated and acidified at the time of collection. Sodium sulfite crystals or a FRESHLY prepared sulfite solution should be used for dechlorination. Following dechlorination, the sample is acidified to a pH < 2 using nitric acid in order to preserve the sample. If the bottles must be shipped to the sampling site with the reagents already present in the bottles, then sulfuric acid should be substituted for nitric acid. Department of Transportation (DOT) regulations must be followed when shipping bottles containing sulfite and sulfuric acid.

**UV Absorbance.** There is not a standardized method for this parameter. The technique originally used to establish a relationship between raw water UV absorbance and THM formation involved filtering the sample through a 0.45 $\mu$ m pore size filter and then measuring UV absorbance at 254 nm. The filter must be prewashed to remove water-soluble organics. EPA will accept information concerning the applicability of alternative procedures for defining this measurement.

EPA is evaluating its data to determine the relationship between TOC and UV absorbance. It may be necessary to measure both parameters in order to better characterize raw water quality.

EPA will accept data demonstrating interferences to the UV measurement at 254 nm that would prevent its use in specific raw waters.

#### **General Comments:**

EPA knows the laboratory capacity for doing DBP compliance monitoring samples is not yet in place. However, EPA believes the capacity can be developed by the time monitoring requirements take effect. PE samples will be available for all the DBPs during 1992, so laboratories can take advantage of those opportunities to demonstrate competency. Part of the laboratory certification process will involve successful performance in PE studies. Laboratories can request PE samples through their State Certification Officer and participation is free.

EPA does not have interlaboratory method performance data for the non-THM DBP methods. EPA anticipates that good

laboratories will be able to achieve quantitative results on analyses of PE samples that are within at least  $\pm 40\%$  of the sample's true value for the non-THM DBPs. However, this has yet to be demonstrated. Some performance data will be generated using the results from PE studies. EPA will also examine alternatives ways to obtain the data, such as round robin studies among several laboratories currently analyzing drinking water samples for DBPs.

The most recent PE studies that included the THMs indicated that the majority of the laboratories participating in the studies were able to achieve results within  $\pm 20\%$  of the THM sample's true value. Therefore, EPA will continue to require that level of performance for certification for THM analyses.

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Table 1. Methods Being Considered for Use in Compliance Monitoring of Disinfectant Residuals Under the D/DBP Rule

Residual	Methodology	Std Meth <sup>*</sup>	Working Range (mg/L)
Free Chlorine	Amperometric Titration	4500-Cl D	≥ 0.1
	DPD Ferrous Titrimetric	4500-Cl F	≥ 0.1
	DPD Colorimetric	4500-Cl G	≥ 0.1
	Syringaldazine (FACTS)	4500-Cl H	≥ 0.1
Total Chlorine	Amperometric Titration	4500-Cl D	≥ 0.1
	Amperometric Titration	4500-Cl E	≤ 0.2
	DPD Ferrous Titrimetric	4500-Cl F	≥ 0.1
	DPD Colorimetric	4500-Cl G	≥ 0.1
	Iodometric Electrode	4500-Cl I	≥ 0.1
Chlorine Dioxide	Amperometric Titration	4500-ClO <sub>2</sub> C	≥ 0.1
	DPD Method	4500-ClO <sub>2</sub> D	≥ 0.1
	Amperometric Titration (proposed)	4500-ClO <sub>2</sub> E	≥ 0.1

\* Method Number Used in the 17th and 18th Editions of *Standard Methods*.

Table 2. Methods Being Considered for Use in Compliance Monitoring of Disinfection By-Products Under the DBP Rule

Residual	Methodology <sup>*</sup>	EPA Method (Ref) <sup>**</sup>	Working Range <sup>†</sup> (µg/L)
Trihalomethanes	P&T/GC/ElCD & PID	502.2 (9)	≥ 2.0
	P&T/GC/MS	524.2 (10)	≥ 0.5
	LLE/GC/ECD	551 (11)	≥ 0.5
Chloral Hydrate	LLE/GC/ECD	551 (11)	≥ 0.5
Haloacetic Acids	LLE or SPE /GC/ECD	552 (10&11)	≥ 5.0
Chlorite & Chlorate IC		300.0 Part B (15)	≥10 <sup>††</sup>
Bromate	IC	300.0 Part B (15)	≥10 <sup>††</sup>

<sup>\*</sup> P&T = purge and trap; GC = gas chromatography; ElCD = electrolytic conductivity detector; PID = photoionization detector; MS = mass spectrometer; LLE = liquid/liquid extraction; ECD = electron capture detector; SPE = solid phase extraction; IC = ion chromatography

<sup>\*\*</sup> Reference for method is given in ().

<sup>†</sup> The concentrations listed in this table are estimates of the lowest levels laboratories can routinely measure with confidence. For methods involving multianalytes (e.g., THM methods), the range is given for the analyte with the highest detection/quantitation level.

<sup>††</sup> Based on experience in EPA's laboratory using a borate eluent. These levels may be optimistic for many drinking water laboratories.