

which is suitable for compliance monitoring. EPA also determined that the newer editions of Standard Methods did not change the individual methods approved under the Stage 1 DBPR.

### 3. Which New Methods Are Proposed for Approval?

a. *EPA Method 327.0 for chlorine dioxide and chlorite.* EPA is proposing to add a new method for the measurement of chlorine dioxide residuals and daily chlorite concentrations. EPA Method 327.0 (USEPA 2003q) is an enzymatic/spectrophotometric method in which a total chlorine dioxide plus chlorite concentration is determined in an unsparged sample and the chlorite concentration is determined in a sparged sample. The chlorine dioxide concentration is then calculated by subtracting the chlorite concentration from the total.

The pH of the samples (sparged and unsparged) and blank are adjusted to 6.0 with a citric acid/glycine buffer. The chromophore Lissamine Green B (LGB) and the enzyme horseradish peroxidase are added. The enzyme reacts with the chlorite in the sample to form chlorine dioxide which then reacts with the chromophore LGB to reduce the absorbance at 633nm of the sample. The absorbance of the samples and blank are determined spectrophotometrically. The difference in absorbance between the samples and the blank is proportional to the chlorite and total chlorine dioxide/chlorite concentrations in the samples.

EPA Method 327.0 offers advantages over the currently approved methods in that it is not subject to positive interferences from other chlorine species and it is easier to use.

The single laboratory detection limits presented in the method are 0.08–0.11 mg/L for chlorite and 0.04–0.16 mg/L for chlorine dioxide. The detection limits are based on the analyses of sets of seven replicates of reagent water that were fortified with low concentrations of chlorite with and without the presence of chlorine dioxide and low concentrations of chlorine dioxide with and without the presence of chlorite. The standard deviation of the mean concentration for each set of samples

was calculated and multiplied by the student's t-value at 99% confidence and n–1 degrees of freedom (3.143 for 7 replicates) to determine the detection limit. The accuracy reported in the method for laboratory fortified blanks at concentrations of 0.2–1.0 mg/L is 103–118 % for chlorite and 102–124 % for chlorine dioxide with relative standard deviations between 2.9 and 16 %. Replicate analyses of drinking water samples from surface and ground water sources fortified at concentrations of approximately 1 and 2 mg/L chlorite and chlorine dioxide showed average recoveries of 91–110 % with relative standard deviations of 1–9 %.

EPA is proposing to approve EPA Method 327.0 as an additional method for monitoring chlorine dioxide and for making the daily determination of chlorite at the entry point to the distribution system. It will provide water systems with additional flexibility in monitoring the application of chlorine dioxide. EPA believes that many water plant operators will prefer the new method over the currently approved methods due to its ease of use.

b. *EPA Method 552.3 for HAA5 and dalapon.* EPA is proposing to add a new method (EPA Method 552.3) for HAA5 that provides comparable sensitivity, accuracy, and precision to the previously approved methods. EPA Method 552.3 (USEPA 2003p) has the added benefit of allowing laboratories to more easily measure four additional haloacetic acids (bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid, and tribromoacetic acid) at the same time the HAA5 compounds are being measured, without compromising the quality of data for the HAA5 compounds. Of the currently approved methods for HAA5, only EPA Method 552.2 (USEPA 1995) provides method performance data for all of these additional compounds, but the reaction conditions must be carefully controlled. EPA believes that analyses for these additional HAAs can be accomplished more easily without compromising the quality of data for the HAA5 compounds by using EPA Method 552.3.

EPA Method 552.3 for HAA5, other haloacetic acids, and the regulated contaminant dalapon allows two extraction options. The first option involves an acidic extraction with methyl tertiary butyl ether (MTBE) which is the same solvent used in the currently approved HAA5 methods. The analytes (HAA5, other HAAs, and dalapon) are then converted to their methyl esters by the addition of acidic methanol to the extract followed by heating. The amount of acidic methanol that is added to the extract is increased in the new method resulting in increased methylation efficiency for some of the analytes. The increased methylation efficiency is significant for the additional HAAs and thus provides greater sensitivity, precision, and accuracy for them when compared to EPA Method 552.2. The acidic extract is neutralized with a saturated solution of sodium bicarbonate and the target analytes are identified and measured by gas chromatography using electron capture detection (GC/ECD).

The second option in the new EPA Method 552.3 involves an acidic extraction with tertiary amyl methyl ether (TAME). The HAAs are then converted to their methyl esters by the addition of acidic methanol to the extract followed by heating. The use of TAME instead of MTBE as the extraction solvent allows the use of a higher temperature during the methylation process. This increases the methylation efficiency and thus provides significant increases in sensitivity, precision, and accuracy for the additional HAAs. The acidic extract is neutralized with a saturated solution of sodium bicarbonate and the target analytes are identified and measured by gas chromatography using electron capture detection (GC/ECD).

The performance of EPA Method 552.3 is comparable to the currently approved methods for determining the HAA5 analytes. A comparison of the performance of EPA Method 552.3 to the currently approved HAA5 methods is shown in Table V–16. The data are taken from the individual methods, so the precision, accuracy, and detection data were not generated using the same samples or by the same laboratory.

TABLE V–16.—PERFORMANCE OF HALOACETIC ACID METHODS

QC Parameter	MCAA	DCAA	TCAA	MBAA	DBAA
Precision (Max %RSD in fortified drinking water samples) <sup>1</sup>					
EPA 552.1 .....	15	14	28	11	7
EPA 552.2 .....	13	6	15	6	5
EPA 552.3 (MTBE option) .....	6	4	1	4	5
EPA 552.3 (TAME option) .....	10	4	2	4	5
SM 6251 B .....	8	7	6	8	7