

passes through the conductivity detector, it enters a postcolumn reactor chamber in which *o*-dianisidine dihydrochloride (ODA) is added to the sample. This compound forms a chromophore with the bromate that is present in the sample and the chromophore concentration is determined using a ultraviolet/visible (UV/Vis) absorbance detector. There are several advantages of this method:

(1) Very few ions react with ODA to form compounds that are detected by the UV/Vis detector. This makes the method less susceptible to interferences for bromate.

(2) The UV/Vis detector is very sensitive to the chromophore, so lower concentrations of bromate can be detected and quantitated. (Bromate concentrations can be reliably quantitated as low as 1 µg/L using this detector versus 5 µg/L for EPA Method 300.1.)

(3) Since the front part of the analysis is the same as EPA Method 300.1, bromate, chlorite, and bromide can be determined in the same analysis.

The first version of this method, EPA Method 317.0 has been evaluated in a multiple laboratory study (Wagner *et al.* 2001; Hautman *et al.* 2001). The results from the study indicate high precision and very low bias in data generated using this method. The interlaboratory precision for bromate, chlorite, and bromide using the conductivity detector and bromate using the UV/Vis detector are 12%, 4.2%, 6.9%, and 9.6% relative standard deviation (RSD), respectively. The interlaboratory bias for bromate, chlorite, and bromide using the conductivity detector and bromate using the UV/Vis detector are 0.35%, -0.98%, -0.87%, and 4.8%, respectively. The average detection levels for bromate, chlorite, and bromide using the conductivity detector and bromate using the UV/Vis detector are 2.2, 1.6, 2.8, and 0.24 µg/L, respectively.

Subsequent to the interlaboratory study of EPA Method 317.0, a problem with ODA was discovered. The purity of the reagent can vary from lot to lot and this affects the performance of the method. EPA has evaluated the method performance using ODA obtained from several commercial sources and from different lots from the same supplier. Based on that new information, EPA revised Method 317.0 to document how to detect and correct problems that can result from a contaminated ODA supply. The revised method is designated EPA Method 317.0 Revision 2.0 and this is the version that is being proposed today. The performance of the revised method is identical to the original version.

EPA believes EPA Method 317.0 Revision 2.0 should be approved as an additional method for bromate, chlorite, and bromide compliance monitoring. EPA anticipates that water systems will prefer to have their bromate samples analyzed by this new method, because it provides higher quality data than the currently approved method when bromate concentrations are below the MCL of 0.010 mg/L (10 µg/L). Only a few laboratories are currently performing analyses using the postcolumn reactor technology included in the method, but the number is increasing as more laboratories become aware of the advantages.

e. *EPA Method 326.0 for bromate, chlorite, and bromide.* EPA Method 326.0 (USEPA 2002a) is based on the procedure reported by Salhi and von Gunten (1999) and uses an approach that is similar to EPA Method 317.0 Revision 2.0. The method involves the separation of the anions (bromate, chlorite, and bromide) following the scheme outlined in EPA Methods 300.1 and 317.0 Revision 2.0. (Bromate, chlorite, and bromide data from the conductivity detector are equivalent to data generated using EPA Method 300.1.) The eluent stream exiting the conductivity detector is mixed with a postcolumn reagent consisting of an acidic solution of potassium iodide with a catalytic concentration of molybdenum (VI). Bromate reacts with the iodide to form triiodide which is measured by its UV absorption at 352 nm.

EPA Method 326.0 has similar accuracy, precision, and sensitivity for bromate compared to EPA Method 317.0 Revision 2.0. Thirty drinking water samples fortified with 1–7 µg bromate/L were analyzed using both methods. Accuracy, expressed as % recovery, ranged from 78.0 to 129% for both methods and precision, expressed as % RSD ranged from 3.7 to 13.5% (Wagner *et al.* 2002). The detection limit of EPA Method 326.0 is 0.17 µg/L as determined by analyzing seven or more replicates of reagent water that is fortified with low concentrations of bromate. The standard deviation of the mean bromate concentration is calculated and multiplied by the student's *t*-value at 99% confidence and *n*-1 degrees of freedom (3.143 for 7 replicates).

EPA is proposing EPA Method 326.0 as an additional method for bromate, chlorite, and bromide compliance monitoring. It provides higher quality bromate data than the currently approved EPA Method 300.1 when bromate concentrations are below 10 µg/L. EPA anticipates the number of

laboratories using this method will increase as utilities become aware of the method's sensitivity and begin to request it be used for their samples.

f. *EPA Method 321.8 for bromate.* EPA is proposing to add EPA Method 321.8 (USEPA 2000d) specifically for bromate compliance monitoring. It involves an ion chromatograph coupled to an inductively coupled plasma mass spectrometer (IC/ICP-MS). The ion chromatograph separates bromate from other ions present in the sample and then bromate is detected and quantitated by the ICP-MS. Mass 79 is used for quantitation while mass 81 provides isotope ratio information that can be used to screen for potential polyatomic interferences. The advantage of this method is that it is very specific and sensitive to bromate. The single laboratory detection limit presented in the method is 0.3 µg/L. The average accuracy reported in the method for laboratory fortified blanks is 99.8% recovery with a three sigma control limit of 10.2%. Average accuracy and precision in fortified drinking water samples are reported as 97.8% recovery and 2.9% relative standard deviation, respectively.

During the Information Collection Rule, thirty-three samples were analyzed by this method in addition to the selective anion concentration (SAC) method used by EPA for the low-level bromate analyses. EPA Method 321.8 provided comparable data to that generated by the SAC method (Fair 2002).

EPA Method 321.8 has undergone second laboratory validation (Day *et al.* 2001) and the results indicate the method can be successfully performed in non-EPA laboratories. The calculated detection limit determined by the second laboratory is 0.4 µg/L. The average accuracy achieved for laboratory fortified blanks at 5 µg/L is 93% recovery with a relative standard deviation of 8.9%. Average accuracy and precision in fortified drinking water samples are reported as 101% recovery and 9% relative standard deviation, respectively.

The IC/ICP-MS instrumentation used in EPA Method 321.8 is a new technology in the drinking water laboratory community. Even though the technology is not yet widely used, EPA believes that approving this new method will provide laboratories with the flexibility to adopt the new technology if they have additional applications for it. The instrumentation is especially promising in the area of trace metal speciation. Laboratories that are performing that type of analysis would find it very useful to also be able