

to perform bromate compliance monitoring analyses by EPA Method 321.8. EPA believes that advances in analytical technology should be encouraged when they provide additional options for obtaining accurate and precise data for compliance monitoring. Approval of this method would not require laboratories to adopt the new technology; it strictly offers the choice for laboratories that would like to use the latest technology.

EPA is proposing to add sample collection and holding time requirement to EPA Method 321.8. The current method does not address the potential for changes in bromate concentrations after the sample is collected as a result of reactions with hypobromous acid/hypobromite ion. Hypobromous acid/hypobromite ion are intermediates formed as byproducts of the reaction of either ozone or hypochlorous acid/hypochlorite ion with bromide ion. If not removed from the sample matrix, further reactions may form bromate ion. The reactions can be prevented by adding 50 mg of ethylenediamine (EDA)/L of sample. This is the preservation technique specified in the other methods both approved and proposed for bromate compliance analyses. The fortified drinking water samples analyzed in the second laboratory validation study of EPA Method 321.8 (Day *et al.* 2001) and the Information Collection Rule samples that were analyzed using the SAC method and EPA Method 321.8 were preserved with EDA, thus demonstrating that EDA can be used in samples analyzed by IC/ICP-MS. EPA believes that adding this sample preservation requirement to EPA Method 321.8 will help ensure sample integrity. It will also simplify the sampling protocols that water systems must follow, because all sampling for bromate, regardless of the method employed to analyze the sample, will require the same sample preservation technique.

EPA Method 321.8 does not include information concerning how long a sample may be stored prior to analysis. EPA is proposing to specify a maximum of 28 days for the sample holding time. This would make the method consistent with the other bromate methods proposed today and the method that is currently approved.

g. *EPA 415.3 for TOC and SUVA (DOC and UV₂₅₄)*. Today's rule proposes to add EPA Method 415.3 (USEPA 2003r) as an approved method for TOC and SUVA. The Stage 1 DBPR included three Standard Methods for TOC and one method for UV₂₅₄. Additional

quality control (QC) requirements were included for these measurements, because the methods did not contain the necessary criteria. The rule included instructions for calculating SUVA based on UV₂₅₄ and DOC analyses. The new EPA Method 415.3 includes the additional QC necessary to achieve reliable determinations for TOC, DOC, and UV₂₅₄. It describes a procedure for removing inorganic carbon from the sample prior to the organic carbon analysis. The method uses the same technologies as already approved. The advantage of this new method is that it documents the precision and accuracy that can be expected when proper QC procedures are implemented and it places all the necessary information for SUVA in one place.

EPA Method 415.3 provides sensitivity, precision and accuracy data for TOC and DOC measured using five different technologies:

- (1) Catalyzed 680°C combustion oxidation of organic carbon to carbon dioxide (CO₂) followed by nondispersive infrared detection (NDIR).
- (2) High temperature (700 to 1100°C) combustion oxidation followed by NDIR.
- (3) Elevated temperature (95–100°C) catalyzed persulfate digestion of organic carbon to CO₂ followed by NDIR.
- (4) UV catalyzed persulfate digestion followed by NDIR.
- (5) UV catalyzed persulfate digestion followed by membrane permeation into a conductivity detector.

These technologies are included in the currently approved Standard Methods 5310 B and 5310 C (APHA, 1996). The new method indicates these technologies can provide detection limits between 0.02 mg/L and 0.12 mg/L. Accuracy and precision data from analyses of fortified reagent water and natural waters indicate the technologies can produce acceptable data for determining compliance with the treatment technique for control of disinfection byproduct precursors specified in § 141.135. Seven natural waters were fortified with organic carbon from potassium hydrogen phthalate and analyzed by each of the five technologies. The average recoveries ranged from 97% to 103% for TOC and 98% to 106% for DOC.

The method presents data from the analyses of seven different waters and demonstrates that comparable analytical results are obtained regardless of the technology used as long as all inorganic carbon is removed from the sample prior to the analysis. The samples ranged in concentration from 0.4 to 3.6

mg/L and the relative standard deviations across the analyses ranged from 35% RSD (for the lowest concentration sample) to ≤13% RSD for the remainder of the samples.

EPA Method 415.3 includes a procedure to ensure that inorganic carbon does not interfere with the organic carbon analyses. Since this is critical to obtaining accurate organic carbon determinations, EPA is proposing to add a requirement at §§ 141.131(d)(3) and (4)(i) to remove inorganic carbon prior to performing TOC or DOC analyses. Laboratories will have the option of using the procedure described in EPA Method 415.3 or verifying that the process used by their TOC instrument adequately removes the inorganic carbon prior to the organic carbon measurement. Determination of organic carbon by subtracting the inorganic carbon from the total carbon is not acceptable for compliance purposes, because the percentage of inorganic carbon is usually large in relation to the organic carbon of the sample and the subtraction process introduces a large potential for error.

The manufacturer of one of the instruments that was used during the development of EPA Method 415.3 recommends that hydrochloric acid be used to acidify TOC and DOC samples prior to analysis. EPA confirmed that use of this acid is critical for proper operation of the instrument. However, use of hydrochloric acid is in conflict with the current regulation at §§ 141.131(d)(3) and (4)(i) which specify phosphoric or sulfuric acid. The type of acid used to preserve samples and to treat the samples to remove inorganic carbon prior to the organic carbon analysis should be based on the analytical method or the instrument manufacturer's specification. Therefore, EPA is proposing to remove the specification of acid type from §§ 141.131(d)(3) and (4)(i).

EPA Method 415.3 specifies that TOC samples be acid preserved at the time of collection in order to prevent microbial degradation of the organic carbon. This is consistent with the sampling instructions in the currently approved methods (Standard Methods 5310 B, 5310 C, and 5310 D). EPA proposes to amend § 141.131(d)(3) by removing the phrase "not to exceed 24 hours" in the description of when samples must be preserved, so that the rule is consistent with the method specifications.

Analyses for both DOC and UV₂₅₄ are required for a SUVA determination. The DOC measurement is identical to the TOC measurement after the sample is filtered through a 0.45 µm pore size filter. The filtration step must be