United States Environmental Protection Agency

Office of Water (4601)

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INITIAL DISTRIBUTION SYSTEM EVALUATION GUIDANCE MANUAL

FOR THE FINAL STAGE 2 DISINFECTANTS AND DISINFECTION BYPRODUCTS RULE

APPENDIX C

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http://www.epa.gov/safewater/disinfection/stage2/compliance.html

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Appendix C

TTHM and HAA5 Sampling Protocol

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C.1 Introduction

It is important that TTHM and HAA5 samples are properly collected and analyzed to ensure accurate analytical results. For example, THMs are volatile chemicals, meaning they can move from the liquid phase to the gas phase under ambient conditions. Therefore, care must be taken to make sure that no air bubbles are present in the filled sample vial. This appendix summarizes information on proper sample collection, handling, and laboratory analytical techniques.

C.2 Analytical Methods

Exhibit C.1 lists the analytes that are included in TTHM and HAA analyses.

Exhibit C.1 TTHM and HAA Analytes

Analyte Group Code	Analytes in Group (Abbreviation for Analyte)
HAA5	Haloacetic acids: Dibromoacetic acid (DBAA) Dichloroacetic acid (DCAA) Monobromoacetic acid (MBAA) Monochloroacetic acid (MCAA) Trichloroacetic acid (TCAA)
HAA9	HAA5 plus four additional analytes Bromochloroacetic acid (BCAA) Bromodichloroacetic acid (BDCAA) Chlorodibromoacetic acid (CDBAA) Tribromoacetic acid (TBAA)
TTHM	Trihalomethanes: Bromodichloromethane (BDCM) Bromoform (CHBr3) Chloroform (CHCl3) Dibromochloromethane (DBCM)

Exhibit C.2 lists the approved laboratory analytical methods for TTHM and HAA5 along with guidelines for sample collection and storage. These guidelines include type of sample container, preservative and dechlorinating agents, pH, and sample collection.

Exhibit C.2 Sampling Requirements of TTHM and HAA5 Analyses

Analyte Group	Analytical Method[1]	Sample Container Material[2]	Preservative/Dechlorinating Agent (Recommended amount)	Storage Guidelines	Sample Collection Guidelines
TTHM	EPA 502.2	40 mL -120 mL screw cap glass vials with PTFE-faced silicone septum	Options: (1) 3 mg $Na_2S_2O_3$/40 mL sample or (2) 3 mg $Na_2S_2O_3$/40 mL sample and immediate acidification using HCl to pH < 2 or (3) 25 mg ascorbic acid/40 mL sample and immediate acidification using HCl to pH < 2. Option 1 may be used if THMs are the only compounds being determined in the sample. Options 2 & 3 require the sample to be dechlorinated prior to the addition of acid.	Keep at 4°C. 14 days maximum hold time[3].	Fill bottle to just overflowing but do not flush out preservatives. No air bubbles. Do not overfill. Seal sample vials with no head space. If ascorbic acid is used to dechlorinate TTHM samples, then the samples MUST be acidified. Acidification of TTHM samples containing $Na_2S_2O_3$ is required if the samples will also be analyzed for VOCs. In both cases, the pH must be adjusted at the time of sample collection, not later at the laboratory.
	EPA 524.2	40 mL -120 mL screw cap glass vials with Teflon-faced silicone septum			
	EPA 551.1	60 mL screw cap glass vials with PTFE-faced silicone septum	1 g phosphate buffer & NH_4Cl or Na_2SO_3 mixture per 60 mL sample (mixture consists of 1 part Na_2HPO_4, 99 parts KH_2PO_4, and 0.6 parts NH_4Cl or Na_2SO_3. 1g per 60 mL results in a pH of 4.8-5.5 and 0.1 mg NH_4Cl or Na_2SO_3 per mL of sample.)		
HAA5	EPA 552.1	250 mL (approx.) amber glass bottles fitted with Teflon-lined screw caps	0.1 mg NH_4Cl per mL of sample		
	EPA 552.2	50 mL (approx.) amber glass bottles fitted with Teflon-lined screw caps			
	EPA 552.3[4]	50 mL (approx.) amber glass bottles fitted with Teflon-lined screw caps			
	SM 6251 B	40 mL or 60 mL screw cap glass vials with PTFE-faced silicone septum	65 mg NH_4Cl		

[1] (40 CFR 141.131 (b))
[2] Selection of container should be coordinated with the laboratory.
[3] The holding time has been changed to 14 days for all HAA5 samples as a part of the Stage 2 DBPR.
[4] EPA Method 552.3 has been added as an approved HAA5 method as part of the Stage 2 DBPR.

C.2.1 Sampling Procedure

It is important to follow sampling procedures provided by your certified laboratory. Sampling procedures may vary slightly among individual laboratories; you should contact your laboratory to learn their procedures. The following is a common procedure for collecting samples for TTHM and HAA5 analyses.

You will need:

1) Sample vials provided by laboratory (most laboratories will provide sample vials with proper preservative and dechlorinating agents)

2) Small bottle of 1:1 hydrochloric acid and eye dropper or pasteur pipette (pH adjustment is necessary for some TTHM methods) (many laboratories will provide ampules with acid for pH adjustment)

3) Water proof labels and permanent (indelible ink) marker

4) Ice/coolant and cooler

Procedure:

1) Label each sample vial. Use waterproof labels and indelible ink. Each label should include:

    - Unique sample ID
    - System name
    - Sample location
    - Sample date and time
    - Analysis required, if not already on label

2) Remove the aerator from the tap, if there is one present.

3) Open the water tap and allow the system to flush until the water temperature has stabilized (usually about 3-5 minutes). The purpose of this step is to ensure the sample does not represent stagnant water that has set for a long time in the water line between the street and the faucet. The sample should be representative of the water flowing through the distribution system at the chosen sampling point.

4) Adjust the flow so that no air bubbles are visually detected in the flowing stream.

5) Slowly fill the sample vial almost to the top without overflowing. Use the bottle cap to add a small amount of additional sample water while simultaneously capping the vial to achieve a headspace-free sample. Be careful not to rinse out any of the preservative/dechlorinating agent during this process. After the bottle is filled, invert three or four times.

6) If collecting TTHM samples that require acidification, let the sample set for about 1 minute, allowing the dechlorinating chemical to take effect. Carefully open the vial and adjust the pH of the TTHM sample to < 2 by adding approximately 4 drops of hydrochloric acid for every 40 mL of sample (amount of acid needed will depend on buffering capacity of sample). Recap the vial, and invert three or four times.

7) Invert the vial and tap it to check for air bubbles. If bubbles are detected, carefully open the vial and add more sample water using the cap to achieve a headspace-free sample.

8) Immediately cool the samples to 4°C by placing them in a cooler with frozen refrigerant packs or ice, or in a refrigerator. Samples should be maintained at this temperature during shipment to the laboratory.

9) Complete the Sample Chain of Custody provided by the laboratory and include it with the sample shipment.

C.2.2 Regarding Loss of Samples

Samples may be "lost" due to a number of reasons:

- Bottle broken during shipment from the water system to the laboratory
- Sample improperly collected (e.g., sample bottle not completely filled)
- Sample improperly shipped (e.g., not kept cold during shipment)
- Sample improperly preserved (e.g., not dechlorinated)
- Bottle is broken or lost at the laboratory
- Quality control doesn't meet method specifications when sample is analyzed

You should conduct resampling for the lost sample as soon as possible after the loss is determined. Only the lost sample needs to be recollected, not the entire sample set that was collected together. Make sure to note the loss of sample and resample date as a deviation in your IDSE report.

C.3 Analytical Method Descriptions

The following are brief summaries of the approved TTHM and HAA5 methods.

C.3.1 EPA Method 502.2

Highly volatile compounds with low water solubility, including TTHMs, are extracted from the water sample by bubbling an inert gas through 5 mL of the sample. The chemical compounds that are extracted from the water sample are then trapped in a tube that contains material to which the chemicals attach, or sorb. Once the extraction process has been completed, the tube containing the extracted chemicals is heated and backflushed with helium, and the mixture of helium and chemicals enters a capillary gas chromatography (GC) column. The column is temperature programmed to separate the chemicals extracted from the water, which are then detected with a photoionization detector (PID) and an electrolytic conductivity detector (ELCD) placed in series. The amount of each chemical is determined using procedural standard calibration. The PID is not required if only TTHMs are being measured.

Chemical compounds are identified by comparing the retention times of unknown GC peaks with retention times for chemical standards analyzed under the same conditions. Confirmation can be made by comparing the relative response from the two detectors. For absolute confirmation of results, a gas chromatography/mass spectrometry (GC/MS) determination can be made using U.S. EPA Method 524.2.

For a complete description of this method see EPA publication: EPA/600/R-95/131 *Methods for the Determination of Organic Compounds in Drinking Water: Supplement III*.

C.3.2 EPA Method 524.2

Volatile organic compounds, including TTHMs, are extracted from the water sample by bubbling an inert gas through the sample. Extracted compounds are trapped in a tube that contains material to which the chemicals attach, or sorb. When the extraction process is complete, the tube is heated and backflushed with helium to de-sorb the trapped chemicals into a capillary gas chromatography (GC) column interfaced with a mass spectrometer (MS). The GC column is temperature programmed to allow for the separation of different chemicals, which are then detected with the MS. Compounds detected by the MS are identified by comparing their measured mass spectra and retention times with reference mass spectra and retention times in a database. Reference mass spectra and retention times for different compounds are obtained by measuring calibration standards under the same conditions that are used for the water samples. The concentration of each compound is measured by comparing the MS response of the compound with the MS response of another compound used as an internal standard. Surrogate chemicals, whose concentrations are known in every sample, are measured using the same internal standard calibration procedure.

For a complete description of this method see EPA publication: EPA/600/R-95/131 *Methods for the Determination of Organic Compounds in Drinking Water: Supplement III*.

C.3.3 EPA Method 551.1

A 50 mL volume of the sample is extracted using either 3 mL of methyl-tert-butyl ether (MTBE) or 5 mL of pentane. A small sub-sample of the extract (2 µL) is then injected into a GC equipped with a fused silica capillary column for separation, and a linearized electron capture detector for analysis. Concentrations of different chemical compounds are determined by comparing their measured amounts to procedural standard calibration curves.

A typical sample can be extracted and analyzed using this method in 50 minutes for chlorination byproducts (e.g., TTHM) and chlorinated solvents, and in two hours for all of the compounds analyzed by this method. Results can be confirmed by using a dissimilar GC column or by the use of GC/MS.

For a complete description of this method see EPA publication: EPA/600/R-95/131 *Methods for the Determination of Organic Compounds in Drinking Water: Supplement III*.

C.3.4 EPA Method 552.1

A 100 mL volume of the sample is adjusted to pH 5.0 and extracted using a pre-conditioned miniature anion exchange column. The chemical compounds to be analyzed are first eluted using small amounts of acidic methanol, and are then esterified directly in this medium after adding a small volume of methyl-tert-butyl ether (MTBE) as a co-solvent. The methyl esters are partitioned into the MTBE phase, and are identified and measured using capillary column gas chromatography with an electron capture detector (GC/ECD).

For a complete description of this method see EPA publication: EPA/600/R-92/129 *Methods for the Determination of Organic Compounds in Drinking Water: Supplement II.*

C.3.5 EPA Method 552.2

The pH of a 40 mL volume of sample is adjusted to less than 0.5, and the sample is extracted using 4 mL of methyl-tert-butyl ether (MTBE). The haloacetic acids that have been partitioned are then converted to their methyl esters by adding acidic methanol and heating them slightly. The acidic extract is then returned to neutral pH using a saturated solution of sodium bicarbonate. The chemical compounds of interest are identified and measured using capillary column gas chromatography with an electron capture detector (GC/ECD). Chemical concentrations are determined using standard calibration procedures.

For a complete description of this method see EPA publication: EPA/600/R-95/131 *Methods for the Determination of Organic Compounds in Drinking Water: Supplement III*.

C.3.6 EPA Method 552.3

The pH of a 40 mL sample is adjusted to 0.5 or less using concentrated sulfuric acid. The sample is then extracted with either methyl tert-butyl ether (MTBE) or tert-amyl methyl ether (TAME) containing an internal standard. The haloacetic acids that have been partitioned are converted to their methyl esters by adding acidic methanol followed by heating for two hours. Sodium sulfate is added to separate the partitioned methylated haloacetic acids from the acidic methanol and the aqueous layer is discarded. The extract is neutralized with a saturated solution of sodium bicarbonate and the solvent layer is removed for analysis. A gas chromatograph equipped with a capillary column and an electron capture detector (GC/ECD) is used for analysis. Chemical concentrations are determined using procedural standard calibration.

For a complete description of this method see *Method 552.3 Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Gas Chromatography with Electron Capture Detection Revision 1.0* (EPA 815-B-03-002), available from EPA's website at http://www.epa.gov/safewater/methods/sourcalt.html.

C.3.7 Standard Method 6251 B

The sample is extracted using methyl-tert-butyl ether (MTBE) at an acidic pH. A salting agent is added during the extraction process to increase the extraction's efficiency. Once extracted, compounds are methylated using diazomethane solution to produce methyl ester or other ether derivatives that can be separated in a gas chromatograph. A gas chromatograph equipped with a fused silica capillary column and an electron capture detector (GC/ECD) is used for analysis. Alternative detectors can be used if quality control criteria are met. Calibration standards are extracted, methylated, and analyzed in the same manner as the water samples to compensate for less than 100% recoveries during sample preparation.

For a complete description of this method see *Standard Methods for the Examination of Water and Wastewater: 19th or 20th Edition* published jointly by the APHA, AWWA, and WEF or Standard Methods Online version 6251 B-94 available at http://www.standardmethods.org.

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