EPA Method 501.3 (EPA 500-Serie)

TITLE: Measurement Of Trihalomethanes In Drinking Water With Gas Chromatography/Mass Spectrometry And Selected Ion Monitoring

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ANALYTE:	CAS #
Chloroform	67-66-3
Bromodichloromethane	75-27-4
Chlorodibromomethane	124-48-1
Bromoform	75-25-2
Trihalomethanes	
THM	

INSTRUMENTATION: GC/MS

1.0 Scope and Application

1.1 This method (501.3) provides procedures for identification and measurement of the four regulated (1) trihalomethanes (chloroform, bromoform, bromodichloromethane, and chlorodibromomethane) in finished drinking water, raw source water, or drinking water in any treatment stage. Previously promulgated methods (2), 501.1 and 501.2, involve gas chromatographic separation, identification, and measurement of these specific trihalomethanes after they are removed from the sample matrix. Method 501.2 is an extraction procedure; Methods 501.1 and 501.3 involve removal of trihalomethanes with purge and trap procedures. In Method 501.3, selected ion monitoring with a mass spectrometer is substituted for the halide-specific gas chromatographic detector specified in Method 501.1. Any one of these methods may be used to analyze drinking water for these four trihalomethanes, whose total concentration is called total trihalomethanes.

1.2 With Method 501.3, method detection limits (MDLs) for trihalomethanes are:

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chloroform,           0.06 ug/L;
bromodichloromethane, 0.07 ug/L;
chlorodibromomethane, 0.05 ug/L; and
bromoform,            0.04 ug/L;
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where MDL is the minimum amount that can be measured with 99% confidence that the reported value is greater than zero (3).

2.0 Summary of Method

2.1 Trihalomethanes are removed (purged) from the sample matrix by bubbling helium through the aqueous sample. Purged trihalomethanes and other

sufficiently volatile sample components with sufficiently low water solubility are sorbed onto Tenax-GCR (a porous polymer based on 2,6-diphenyl-p-phenylene oxide) contained in a stainless steel tube. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb purged sample components into a gas chromatograph (GC) interfaced to a mass spectrometer (MS). Trihalomethanes eluting from the GC column are identified and measured by acquiring mass spectral data for selected ions that are characteristic of individual trihalomethanes.

3.0 Interferences and Contamination Sources

3.1 With selected ion monitoring, the mass spectrometer is essentially a compound-selective detector, and interferences are minimal. GC retention time and relative ion abundance data for the four trihalomethanes provide reliable identifications. No known compounds that are purged with the conditions used in this method have the same GC retention times and also produce the same fragment ions in the same relative abundances as the four trihalomethanes.

3.2 With selected-ion monitoring, interfering contamination is only likely to occur when a sample containing low concentrations of trihalomethanes is analyzed immediately after a sample containing relatively high concentrations of trihalomethanes. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of trihalomethanes, the system should be baked for 10 min by passing helium through the sample purging chamber into the heated (180 ˚C) sorbent trap. One or more method blanks should be analyzed to ensure that accurate values are obtained for the next sample.

3.3 Samples may be contaminated during shipment or storage by diffusion of volatile organics through the sample bottle septum seal. Field blanks must be analyzed to determine when sampling and storage procedures have not prevented contamination.

3.4 During analysis, major contaminant sources are impurities in the inert purging gas and in the sorbent trap. Analysis of field blanks and method blanks provides information about the presence of contaminants.

4.0 Safety

4.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited (4,6)

4.2 Primary standards of trihalomethanes should be handled in a hood.

5.0 Equipment and Materials

5.1 Sample containers -- 25-mL or larger glass bottles, equipped with a screw cap with center hole (Pierce #13075 or equivalent) and a Teflon(R) faced silicone septum.

5.2 Purge and trap device (Figures 1-2) consisting of sample purging chamber, sorbent trap and desorber. (Acceptable devices are commercially available.)

5.2.1 The all glass sample purging chamber (Figure 1) holds 5-mL samples with < 15 mL of gaseous headspace between the water column and the trap. The helium purge gas passes through the water column as finely divided bubbles (optimum diameter of <3 mm at the origin). The purge gas must be introduced at a point <S mm from the base of the water column.

5.2.2 The stainless steel sorbent trap (Figure 3) is 25 cm long by 2.5 mm ID and is packed with 1 cm of methyl-silicone coated packing, 15 cm of Tenax-GCR, and 8 cm of silica gel, in that order with respect to the inlet end of the trap. Silica gel is not necessary for efficient trapping of trihalomethanes but does not hinder trapping; therefore, silica gel may be replaced with additional Tenax-GCR. A trap with different dimensions can be used if it has been evaluated and found to perform satisfactorily. Before initial use, the trap should be conditioned overnight at 180 ˚C by backflushing with helium flow of at least 20 mL/min. Each day the trap should be conditioned for 10 min at 180 ˚C with backflushing.

5.2.3 The desorber (Figure 3) should be capable of rapidly heating the trap to 180 ˚C. The trap section containing Tenax-GCR should not be heated to higher than 180 ˚C, and the temperature of the other sections should not exceed 200 ˚C.

5.3 Syringes and syringe valves

5.3.1 Two 5-mL glass hypodermic syringes with Luerlok tip (if applicable to the purging device being used).

5.3.2 One 5-mL gas-tight syringe with shutoff valve.

5.3.3 Two two-way syringe valves with Luer ends (if applicable to the purging device being used).

5.3.4 One 25-uL micro syringe with 0.006 in. ID needle.

5.3.5 One 100-uL micro syringe.

5.4 Miscellaneous

5.4.1 Standard solution storage containers -- 10 mL bottles with Teflon(R)-lined screw caps.

5.4.2 Analytical balance capable of weighing 0.0001 g accurately.

5.4.3 Helium purge gas, as contaminant free as possible.

5.5 Sorbent trap packing materials

5.5.1 Polymer based on 2,6-diphenyl-p-phenylene oxide -- 60/80 mesh Tenax-GCR, chromatographic grade, or equivalent.

5.5.2 Methyl silicone coated packing -- 3% OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.5.3 Silica gel -- 35/60 mesh, Davison Chemical grade 15, or equivalent.

5.6 Reagents

5.6.1 Sodium thiosulfate or sodium sulfite -- granular, ACS reagent grade.

5.6.2 Methanol -- pesticide quality or equivalent.

5.6.3 Reagent water -- water in which an interferant is not observed at the method detection limit of the compound of interest. Reagent-water may be prepared by passing tap water through a filter bed containing about 0.5 kg of activated carbon (Calgon Corp. Filtrasorb 300 or equivalent), by using a water purification system (Millipore Super Q or equivalent), or by boiling distilled water for 15 min followed by a 1 h purge with inert gas while the water temperature is held at 90 ˚C. Reagent water should be stored in clean, narrow-mouth bottles with Teflon(R)-lined septa and screw caps.

5.7 Stock standard solutions -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

5.7.1 Place about 9.8 mL of methanol in a 10-mL ground-glass stoppered volumetric flask. Allow the flask to stand unstoppered for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg. With a 100-uL syringe, immediately add two or more drops of assayed reference compound to the flask. (The liquid must fall directly into the alcohol without contacting the flask.) Reweigh the flask, dilute to volume, stopper, and mix by inverting several times.

5.7.2 From the net weight gain, calculate the concentration in micrograms per microliter. When assayed compound purity is > 96%, the uncorrected weight may be used to calculate concentration.

5.7.3 Stock standard solutions should be stored with minimal headspace in Teflon(R)-lined screw-capped bottles.

5.8 Secondary dilution standard -- Stock standard solutions are used to prepare a secondary dilution standard solution that contains the four trihalomethanes

in methanol. The secondary dilution standard should be prepared at a concentration that can be easily diluted to prepare aqueous calibration solutions (Section 8.2.3) at concentrations that will bracket the working concentration range. (For this method, the concentration of each trihalomethane in the secondary dilution standard solution should be about 1 to 25 ug/mL.) The solution should be stored with minimal headspace and should be checked frequently for signs of deterioration or evaporation, especially just before preparing calibration standards from it.

5.9 Internal standard spiking solution and surrogate compound spiking solution -- A spiking solution of fluorobenzene in methanol should be prepared at a concentration of 0.5 ug/mL. When 10 uL of this solution is added to 5 mL of sample or standard calibration solution, the fluorobenzene concentration will be 1 ug/L. If the internal standard technique is used, fluorobenzene serves as the internal standard. If the external standard technique is used, fluorobenzene is a surrogate compound added to each sample to monitor method efficiency. The measured efficiency for fluorobenzene is considered to be indicative of method efficiency for the four trihalomethanes being measured with this method.

5.10 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

5.10.1 The GC, which must be capable of temperature programming, should be interfaced to the MS with an all-glass enrichment device and an all-glass transfer line. Any enrichment device or transfer line can be used, however, if performance specifications described in this method can be demonstrated with it. The recommended GC column is 1.8 m long by 2 mm ID glass packed with 1% SP-1000 on 60/80 mesh Carbopack B. Helium carrier gas flow rate is 30 mL/min. The column temperature program is initial 3 min period at 45 ˚C, increased to 200 ˚C at a rate of 8 ˚C/min, and isothermal at 200 ˚C for 15 min. Other columns may be used if they provide data with adequate accuracy and precision as specified in this method. An alternative column is 1.8 m long by 2 mm ID glass or stainless steel packed with 0.2% Carbowax 1500 on 80/100 mesh Carbopack C.

5.10.2 Mass spectral data are to be obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must produce a mass spectrum that meets all criteria in Table 1 when 50 ng or less of p-bromofluorobenzene (BFB) is introduced into the GC.

5.10.3 An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The data system must be equipped with a program to acquire data for only a few selected ions that are characteristic of the internal standard and the trihalomethanes being analyzed. As compounds elute from the GC, mass spectral data are acquired continuously, but only for a few masses rather than for a broad mass range that would provide a complete mass spectrum of each sample component. This is known as selected ion monitoring

(SIM).

Table 1. Ion Abundance Criteria for p-Bromofluorobenzene

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	< 2% of mass 174
174	> 50 of mass 95
175	5 to 9% of mass 174
176	> 95% but < 101% of mass 174
177	5 to 9% of mass 176

5.10.4 SIM is used because it provides lower detection limits than does full-spectrum data acquisition. Although identifications based on SIM data are less reliable than those based on full-spectrum data, identifications of the four trihalomethanes are more reliable with SIM than with the most selective conventional chromatographic detectors. This identification reliability is obtained by using relative retention time information, by selecting appropriate characteristic ions to be monitored, and by checking relative abundances of naturally occurring isotopes of chlorine and bromine.

5.10.5 Increased sensitivity is achieved with SIM because more time is dedicated to acquiring abundance data for each mass when only a few masses (ions) are monitored rather than every mass in the full-spectrum mass range. For example, if 4 s are required for full-spectrum data acquisition, approximately 17 ms will be dedicated to each mass from 20 to 260 atomic mass units (amu). If only eight masses are monitored, however, approximately 500 msec can be dedicated to each mass during a 4 s data acquisition period. This relatively long data acquisition time with SIM improves detection limits by averaging random noise, which improves the signal-to-noise ratio.

5.10.6 For SIM of trihalomethanes, the data system must be capable of monitoring at least four ions; the capability to monitor eight ions is highly desirable. When less than eight ions can be monitored simultaneously, this disadvantage can be overcome if the ions being monitored can be changed as a function of time. With knowledge of trihalomethane retention times, the operator can then change ions being monitored as different compounds elute.

6.0 Selection of Ions

6.1 The four trihalomethanes are distinguished from one another and from other

sample components by acquiring abundance information about characteristic ions and by using GC retention time data. Mass spectra of the four trihalomethanes (Figures 4-7) contain characteristic patterns caused by chlorine and bromine isotopes. For example, the chloroform mass spectrum contains an ion cluster at m/z 83, 85, and 87 with known relative abundances of 35Cl and 37Cl isotopes. Similar isotope clusters are produced by fragmentation of molecules containing bromine or chlorine and bromine.

6.2 Because two ions are monitored for each trihalomethane, relative abundances of isotope cluster ions provide corroborating identification information. To achieve maximum sensitivity, monitored ions (Table 2) are the two most abundant ions in a trihalomethane mass spectrum. Because chloroform and bromodichloromethane produce identical isotope clusters at m/z 83, 85, and 87 (produced by loss of chlorine and bromine, respectively), m/z 83 and 85 are used to monitor both compounds. (They are distinguished from each other by differences in retention time.) Two ions each are needed to identify and measure dibromochloromethane and bromoform; one ion is required for fluorobenzene. Therefore, the capability to monitor a total of seven ions is needed to measure simultaneously all four trihalomethanes and fluorobenzene.

Table 2. Ions Selected to Detect and Measure Trihalomethanes

Compound	Ion	m/z	Theoretical Rel. Abun. (%)
CHCl3	CHCl2+	83	100
		85	65
CHCl2Br	CHCl2+	83	100
		85	65
CHClBr2	CHClBr+	127	77
		129	100
C6H5F	C6H5F+	96	100
CHBr3	CHBr2+	171	51
		173	100

6.3 If only four ions can be monitored simultaneously but the set of ions can be changed with only a brief interruption of data acquisition, different compounds can be monitored as they elute from the GC. For example, an ion current profile similar to that obtained when seven ions were monitored (Figure 8) can be obtained by sequentially monitoring two sets of ions, one set of four ions and one of three ions. Monitoring m/z 83, 85, 127 and 129 until after chlorodibromomethane elutes would permit detection of chloroform, bromodichloromethane, and chlorodibromomethane. Changing the set of monitored ions to m/z 96, 171 and 173 would then permit detection of fluorobenzene and bromoform.

6.4 Although some purgeable organohalides have the same retention times as trihalomethanes with the recommended columns, these compounds are not

observed because they do not produce ions being monitored. A representative chromatogram of halogenated organic compounds (Figure 9) shows no components coeluting with chloroform or bromodichloromethane. Chlorodibromomethane, however, coelutes with 1,1,2-trichloroethane and cis-1,3-dichloropropene. Because neither of the latter two compounds produces ions at m/z 127 or 129 (which are the ions used to detect and measure chlorodibromomethane), neither will be observed. A similar situation exists with the coelution of bromoform (monitored with m/z 171 and 173) and 1,1,1,2-tetrachloroethane, which produces neither m/z 171 nor 173.

6.5 Non-halogenated compounds will not be falsely identified as trihalomethanes, because two ions are monitored to detect isotope clusters produced by trihalomethanes, but not by non-halogenated compounds.

6.6 The length of time to be spent acquiring data for each ion must be selected with consideration of several factors, such as the number of ions monitored, total data acquisition time for the set of monitored ions, GC resolution of sample components, ion counting statistics, and dynamic range of ion detection and data storage devices. Sufficient time must be spent on each ion to acquire reliable data about changes in ion abundance as a function of time. If too much time is spent on any one ion, however, other sample components will not be detected as they elute from the GC column. At least five data points must be acquired for each GC peak. The same data acquisition time need not be used for all ions monitored; the data acquisition time used to monitor a sample component, however, must be the same as the time used to prepare the calibration curve for that trihalomethane or to calculate its relative response factor.

7.0 Sample Collection, Preservation and Handling

7.1 All samples should be collected in duplicate. Sample bottles must be filled to overflowing. No air bubbles should pass through the sample as the bottle is filled, or be trapped in the sample when the bottle is sealed. Samples must be kept sealed from collection time until analysis; this storage period should not exceed 14 days, because significant biodegradation may occur after this period.

7.1.1 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized. Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

7.1.2 When sampling from an open body of water, fill a 1-qt wide-mouth bottle with sample from a representative area, and carefully fill duplicate sample bottles from the 1-qt bottle.

7.2 If a sample is expected to contain residual chlorine, a reducing agent, sodium thiosulfate or sodium sulfite (10 mg per 40-mL sample for up to 5 ppm chlorine) should be added to the empty sample bottle before it is

shipped to the sampling site. (The reducing agent is not added to samples to be analyzed to determine maximum trihalomethane potential.)

7.3 Duplicate field blanks must be collected along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. Field blanks are prepared by filling sample bottles with reagent water at the laboratory and shipping the sealed bottles to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. (If reducing agent is added to sample bottles, it must also be added to blanks.)

8.0 Calibration

8.1 The analytical system is calibrated each 8 h period by analyzing standard solutions with the same procedures that will be used to analyze samples (Section 9). Either the external standard or internal standard technique may be used. With either technique, however, fluorobenzene must be added (Section 5.9) to all calibration solutions, because it will be used either as an internal standard or as a surrogate compound.

8.2 External Standard Technique

8.2.1 An external standard is a known amount of a pure compound that is analyzed with the same procedures and conditions that are used to analyze samples containing that compound. From measured detector responses to known amounts of the external standard, a concentration of that same compound can be calculated from measured detector response to that compound in a sample analyzed with the same procedures.

8.2.2 Calibration curves are prepared by analyzing at least three calibration solutions, each containing a standard of each of the four trihalomethanes. One solution should contain each trihalomethane at a concentration approaching but greater than the method detection limit (Table 4) for that compound; the other two solutions should contain trihalomethanes at concentrations that bracket the range expected in samples. For example, if the detection limit for a particular trihalomethane is 0.06 ug/L, and a 5-mL sample expected to contain approximately 5 ug/L is analyzed, aqueous solutions of standards should be prepared at concentrations of 0.1 ng/mL, 1 ng/mL, and 10 ng/mL.

8.2.3 Three calibration solutions are prepared by adding 20.0 uL of the secondary dilution standard solution to 50 mL, 250 mL, and 500 mL aliquots of reagent water. (A 25-uL syringe with a 0.006 in. ID needle is recommended for this transfer.) Aqueous standard solutions may be stored for up to 24 hr in sealed vials with zero headspace.

8.2.4 Because the surrogate, fluorobenzene, will be spiked into all samples by adding 10 uL of the surrogate spiking solution, this technique

should also be used to add the surrogate to calibration solutions. The surrogate spiking solution should be added to the syringe containing 5 mL of calibration solution immediately before the syringe is attached to the purging device.

8.2.5 Each calibration solution is analyzed with the procedures to be used to analyze samples. For each trihalomethane, integrated abundances of the ion characteristic of that compound are plotted as a function of the concentration. The primary (most abundant) characteristic ion should be used (Table 2). If the ratio of ion abundance to amount of trihalomethane is constant (< 10% relative standard deviation) throughout the concentration range, the average ratio may be used instead of a calibration curve.

8.2.6 Calibration data must be checked each day by measurement of one or more external standard calibration solutions. If the absolute ion abundance measured for any trihalomethane varies from expected abundance by more than 10%, a fresh calibration solution must be prepared and analyzed. Preparation of a new calibration curve may be necessary, because detector response may have changed.

8.3 Internal standard technique

8.3.1 An internal standard is a pure compound added to a sample in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not contained in the sample. Fluorobenzene was selected as the internal standard because it:

- is stable in aqueous solutions,
- is efficiently purged from aqueous solutions,
- does not occur naturally,
- is-not commercially produced in bulk quantities but is available as a laboratory reagent chemical,
- does not coelute with any of the trihalomethanes being monitored but elutes among them (Figure 8), and
- can be monitored with one ion.

8.3.2 A calibration curve should be prepared by analyzing at least three aqueous solutions containing a known amount of each of the four trihalomethanes and the internal standard, fluorobenzene. One of the solutions should contain trihalomethane standards at concentrations near the limit of detection; in the other solutions, trihalomethane concentrations should bracket the range of concentrations expected in samples. The internal standard concentration must be constant in all calibration solutions.

8.3.3 Because the internal standard will be spiked into all samples by adding 10 uL of the internal standard spiking solution, this technique must also be used to add the internal standard to calibration solutions. The

internal standard spiking solution is added to the syringe containing 5 mL of calibration solution immediately before the syringe is attached to the purging device.

8.3.4 Trihalomethane measurements are calibrated by calculating the mass spectrometer response to each compound relative to fluorobenzene, the internal standard. The response factor (RF) is calculated with the equation,

$$RF = \frac{A(x) * Q(s)}{A(s) * Q(x)}$$

where:

A(x) = integrated abundance of the selected ion for the trihalomethane standard;
A(s) = integrated abundance of the selected ion for the internal standard;
Q(s) = quantity of internal standard; and
Q(x) = quantity of trihalomethane standard.

RF is a unitless number; units used to express quantities of trihalomethane and internal standard must be equivalent.

8.3.5 For each trihalomethane, the response factor should be independent of trihalomethane quantity for the working range of the calibration. Each day, one or more standards must be analyzed to verify that response factors have not changed. When changes occur (> 10% relative standard deviation), new standard solutions must be prepared and analyzed to determine new response factors.

9.0 Sample Analysis

9.1 Analysis Procedures

9.1.1 Initial conditions -- Adjust the helium purge gas flow rate to 40 +/- 3 mL/min. Attach the sorbent trap to the purging device, and set the device to the purge mode. Open the syringe valve located on the sample introduction needle of the purging chamber.

9.1.2 Sample introduction and purging -- Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. (Because this process of taking an aliquot impairs the integrity of the remaining sample, a second syringe should be filled at the same time, in case a second analysis is required.) Add 10.0 uL of the spiking solution (Section 5.9) of fluorobenzene in methanol through the syringe valve and

close the valve. Attach the syringe and its valve assembly to the syringe valve on the purging device. Open the syringe valves and slowly inject the sample into the purging chamber. Close both valves and purge the sample for 11.0 +/- 0.1 min at ambient temperature.

9.1.3 Desorption and data acquisition -- At the conclusion of purging, attach the sorbent trap to the GC, adjust the purging device to the desorb mode, and initiate the GC temperature programming (Section 5.10.1), trap heating, (Section 5.2) and MS data acquisition (Section 6). Trapped sample components are transferred into the GC column by heating the trap to 180 ˚C rapidly (within 4 min) while it is backflushed with helium flowing at 20 to 60 mL/min. (If the trap cannot be heated rapidly, the GC column may be used as a secondary trap by cooling the column to < 30 ˚C during desorption.)

9.1.4 Sample chamber rinsing -- During desorption empty the purging chamber with the sample introduction syringe, and rinse the chamber with two 5-mL portions of reagent water.

9.1.5 Trap reconditioning - After desorbing the sample for 4 min, reset the purging device to the purge mode. After 15 s, close the syringe valve on the purging device to begin gas flow through the trap. After approximately 7 min, turn off the trap heater and open the syringe valve to stop gas flow through the trap. When cool, the trap is ready for the next sample.

9.1.6 Termination of data acquisition - When sample components have eluted from the GC, terminate MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display selected ion abundance profiles. If any ion abundance exceeds the system working range, dilute the sample aliquot in the second syringe with reagent water and analyze the diluted aliquot.

9.2 Identification criteria

9.2.1 The GC retention time of the sample component trihalomethane must be within t s of the time observed for that same compound when the standard solution was analyzed. The value of t is calculated with the equation:

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t = (RT)^0.5
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where:

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RT = observed retention time (in seconds) of the
     compound when standard solution was analyzed.
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9.2.2 Relative abundances of naturally occurring isotopes must agree with theoretical values within +/- 10% (Table 3).

Table 3. Relative Abundance Criteria for Trihalomethane Ions

Compound	Selected Ions	Abundance Criteria
CHCl3	83 & 85	m/z 85 = 58 to 72% of m/e 83
CHCl2Br	83 & 85	m/z 85 = 58 to 72% of m/e 83
CHClBr2	127 & 129	m/z 127 = 69 to 85% of m/e 129
CHBr3	171 & 173	m/z 171 = 46 to 56% of m/e 173

9.3 Concentration calculations

9.3.1 With either the internal or external standard technique, concentrations are calculated with the equation:

$$C(x) = \frac{A(x) * Q(s)}{A(s) * RF * V}$$

where

C(x) = analyte concentration in micrograms per liter;
A(x) = integrated ion abundance of the primary characteristic ion of the sample analyte;
A(s) = integrated ion abundance of the primary characteristic ion of the standard (either internal or external), in units consistent with those used for the analyte ion abundance;
RF = response factor (With an external standard, RF = 1, because the standard is the same compound as the measured analyte.);
Q(s) = quantity of internal standard added or external standard analyzed, in micrograms; and
V = purged sample volume in liters.

9.3.2 The concentration of total trihalomethanes is the sum of concentrations of the four individual trihalomethanes.

10.0 Quality Control

10.1 Minimum quality control requirements consist of initial demonstration of laboratory analytical capability (efficiency, accuracy and precision procedures, Sections 10.2.7-10.2.9), analysis of laboratory control standards as a continuing performance check, quarterly analysis of a quality control check sample (Section 10.2.11), and maintenance of performance records to define the quality of generated data.

10.2 Quality Control Analyses

10.2.1 *Field blanks* -- A field blank must be analyzed along with each sample set. If a field blank contains trihalomethanes at concentrations above the method detection limits, a method blank must be analyzed. If trihalomethanes are not detected in the method blank but are detected in the field blank, sampling or storage procedures have not prevented sample contamination, and the

sample set must be discarded.

10.2.2 *Method blanks* -- A method blank is a 5-mL portion of reagent water placed in the purging apparatus and analyzed as if it were a drinking water sample. A reagent water blank must be analyzed each day to demonstrate acceptable levels of interferences and contaminants in the analytical system. No sample is to be analyzed until no trihalomethanes are detected in method blanks at concentrations above method detection limits.

10.2.3 *Laboratory duplicates* -- To determine precision associated with laboratory techniques, analyze two aliquots (Section 9.1.2) of at least 5% of the samples in which trihalomethanes were observed at concentrations above method detection limits. Calculate percent deviation (D) of duplicate analyses using the formula:

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      D = (R / C) * 100
where

  C = mean concentration observed, and
  R = range of concentrations observed

  If D is greater than 30%, precision is inadequate,
      and laboratory techniques must be improved.
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10.2.4 *Field duplicates* -- At least 10% of samples should be analyzed in duplicate to determine precision limitations imposed by sampling, transport and storage techniques.

10.2.5 *MS performance standard* -- Near the beginning of each 8 h work period day that trihalomethanes are to be measured, the mass spectrum produced by < 50 ng of p-bromofluorobenzene (BFB) must be measured to ensure that it meets performance criteria (Table 1). BFB may be introduced into the MS either by syringe injection or through the purge and trap system. The entire mass spectrum (mass range 35 to 260 amu) should be obtained at an MS scan rate that produces at least five spectra for the BFB GC peak but does not exceed 7 s per spectrum. If the BFB spectrum is unacceptable, GC/MS operating parameters must be adjusted until an acceptable spectrum is produced before samples are analyzed.

10.2.6 *Laboratory control standard* -- To demonstrate ability to produce data within acceptable accuracy and precision limits, a laboratory control standard must be analyzed during each 8 h work period. A laboratory control standard is reagent water spiked with known amounts of trihalomethanes.

10.2.6.1 For each trihalomethane to be measured, select a concentration representative of its occurrence in drinking water samples. From stock standard solutions, prepare a laboratory control standard concentrate in methanol. This

solution should contain all four trihalomethanes at concentrations 500 times those selected as representative concentrations. (Laboratory control standard concentrates, which are also called QC check sample concentrates, are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio 45268.)
10.2.6.2 Add 10 uL of the laboratory control standard concentrate to a 5-mL aliquot of reagent water, and analyze according to procedures in Section 9.0

10.2.7 *Method efficiency* - For each trihalomethane, method efficiency is calculated by comparing the detector response when the compound is introduced by syringe injection with the detector response when the same amount is introduced by purging, trapping, and desorption. Because of the calibration technique used in this method, high efficiency is not required for acceptable precision and accuracy but is required for acceptable sensitivity. Low method efficiency will cause unacceptably high detection limits. Method efficiency for each trihalomethane must be recalculated when the analytical system undergoes major modification, such as replacement of trap packing.

10.2.7.1 At least five laboratory control standards are analyzed with the purge, trap, desorption and GC/MS SIM detection procedures. Interspersed among these five or more analyses, three or more aliquots of the secondary dilution standard solution (Section 5.8) are injected directly .into the GC to introduce each trihalomethane in an amount equivalent to that introduced by purge and trap procedures. The recommended amount is 5 ng of each trihalomethane. The same MS data acquisition parameters are used for SIM of injected trihalomethanes as are used for those introduced with the purge and trap procedures.

10.2.7.2 Calculate the method efficiency (E) for each trihalomethane in each aliquot of the laboratory control standard with the equation:

$$E = \frac{A(p)}{A(i)} * 100$$

where
A(p) = ion abundance of compound introduced with purge and trap techniques, and
A(i) = ion abundance produced by an equal amount of the same compound when injected.

For this calculation, use data obtained from an injection

either closely preceding or following the purge and trap analysis from which data are used.

10.2.7.3 Calculate the mean method efficiency for each compound and the mean of the mean method efficiencies for all four trihalomethanes. Acceptable detection limits can be achieved if the mean of the mean method efficiencies is >= 60%; the minimum required efficiency for any individual trihalomethane is 30%.

10.2.8 *Accuracy* -- Accuracy can be calculated from the same set of data acquired to determine efficiency. One aliquot of the laboratory control standard analyzed with purge and trap techniques is selected to be treated as a standard with known component concentrations, and the other aliquots are treated as samples. (Data obtained from direct injections are not used in accuracy calculations.) Data acquired for the aliquot chosen to be the standard may be treated as an external standard or may be used to calculate response factors relative to fluorobenzene used as an internal standard.

10.2.8.1 When using the external standard procedure, data obtained from the solution selected as a standard are assumed to be true values, and accuracy is the ion abundance found in the sample solution expressed as a percentage (P) of the ion abundance found in the external standard solution:

$$P = \frac{A(x)}{A(s)} * 100$$

where

A(x) = abundance of ion used to monitor trihalomethane treated as an unknown, and
A(s) = abundance of ion used to monitor the same trihalomethane treated as an external standard.

10.2.8.2 When using the internal standard procedure, fluorobenzene in the solution of trihalomethane standards is selected as an internal standard, and response factors are calculated (Section 8.3.4) for each trihalomethane relative to fluorobenzene. With these response factors, SIM data acquired for the other solutions analyzed are used to calculate accuracy:

$$P = \frac{A(x) * 100}{A(s) * RF}$$

where

A(x) = abundance of ion used to monitor a trihalomethane in the laboratory control standard solution,
A(s) = abundance of ion used to monitor fluorobenzene in the same solution, and
RF = response factor of the particular trihalomethane relative to fluorobenzene.

10.2.8.3 For each of the four trihalomethanes, the mean accuracy is calculated; the mean of these four means is the method accuracy and must be in the range of 90 to 110%.

10.2.9 Precision

10.2.9.1 For each trihalomethane, method precision is expressed as the standard deviation(s) of the percentages of the true values (P) obtained in the accuracy calculations:

$$s = \left[\frac{n \cdot \left(\sum_{i=1}^{n} P(i)^2\right) - \left(\sum_{i=1}^{n} P(i)\right)^2}{n \cdot (n-1)}\right]^{0.5}$$

where

! = summation symbol, and
n = number of measurements for each trihalomethane.

10.2.9.2 The dispersion of the set of means for each trihalomethane is expressed as the relative standard deviation (RSD):

$$RSD = \frac{s}{P} \cdot 100$$

where

s = standard deviation, and

P = mean percentage of true value.

10.2.9.3 Adequate precision is obtained when the relative standard deviation is < 15%.

10.2.10 Monitoring the surrogate compound -- If the external standard technique is used, fluorobenzene is a surrogate compound used to monitor method performance. Each day method efficiency is determined for fluorobenzene by analyzing a laboratory control

standard and comparing results obtained with purge and trap procedures to those obtained with direct injection. If for any sample, method efficiency (Section 10.2.7) and accuracy (Section 10.2.8) values obtained for fluorobenzene fall below acceptable values, trihalomethane values obtained for that sample should not be reported.

10.2.11 At least quarterly, a quality control check sample obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, must be analyzed. If measured trihalomethane concentrations are not within +/- 20% of true values, the entire analytical procedure must be checked to locate and correct the problem source.

11.0 Method Performance

11.1 The method detection limit is defined (3) as the minimum concentration of analyte that can be measured and reported with 99% confidence that the value is above zero. Method detection limits and single laboratory accuracy and precision data (Table 4) were obtained from seven replicate analyses (using the external standard technique) of reagent water spiked with trihalomethanes. For the four trihalomethanes, individual mean method accuracies were calculated, and a mean method accuracy for all four was calculated to be 102.4%.

REFERENCES

1. "National Interim Primary Drinking Water Regulations; Control of Trihalomethanes in Drinking Water," Federal Register, Volume 44, No. 231, p. 68624 (November 29, 1979).

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3. "Definition and Procedure for the Determination of the Method Detection Limit," U. S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, July 1981, Revision 1.12.

4. "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health , Publication No. 77-206, Aug. 1977.

5. "OSHA Safety and Health Standards, General Industry," (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

Table 4. Single Laboratory Accuracy and Precision Data for Selected Ion Monitoring of Trihalomethanes

Compound	CAS Reg No.	Meas. Ion(b)	True Conc. ug/L	Mean Observed Conc(ug/L)	Mean Method Accuracy	Std. Dev. ug/L	Rel. Std. Dev.	MDL (c) ug/L
Chloroform	67-66-3	83	0.200	0.195	97.5	0.019	9.7	0.06
			20	19.0	94.9	2.7	2.8	--
Bromodichloro-methane	75-27-4	83	0.200	0.206	103.0	0.021	10.2	0.07
			20	18.7	93.7	3.4	3.6	--
Chlorodibromo-methane	124-48-1	129	0.200	0.206	103.0	0.016	7.6	0.05
			20	18.2	90.8	5.2	5.8	--
Bromoform	75-25-2	173	0.200	0.212	106.0	0.012	5.8	0.04
			20	18.3	91.5	7.7	8.4	--

(a) Produced by analysis of seven aliquots of reagent water spiked with known amounts of trihalomethanes; calculations based on external standard technique.
(b) Seven ions were monitored for a total integration time of approximately 3.5 sec for each set of ions.
(c) Minimum concentration that can be measured with 99% confidence that reported value is greater than zero (3).