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# Method 524. Measurement of Purgeable Organic Compounds in Drinking Water by Gas Chromatography/Mass Spectrometry

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE FEB 22 1983

SUBJECT Nationwide Approval of Alternate Test Procedure for Analysis of Trihalomethanes

FROM Victor J. Kimm, Director
Office of Drinking Water (WH-550)

TO Regional Administrators

Listed below is an alternate test procedure for determining trihalomethanes by a gas chromatography-mass spectrometry (GC-MS) method which I have approved for nationwide use for "National Interim Primary Drinking Water Regulation" (NIPDWR) compliance monitoring.

This method was developed by the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati for the measurement of purgeable organic compounds in drinking water. Unlike the previously approved Method 501.3 which involves selected-ion monitoring with a mass spectrometer, this method permits the acquisition of complete mass spectra. In addition, this method can be used for the measurement of many other volatile organic compounds along with the trihalomethanes. EMSL's data show that the precision and accuracy of this method is comparable to that of EPA's approved methods. (Previously approved methods for trihalomethanes are 501.1, 501.2 and 501.3.) Although detection limits for trihalomethanes are not as low as those obtained with other approved methodology, they are entirely adequate for the current maximum contaminant level.

| Measurement | Method |
|---|---|
| Total Trihalomethanes | [1]Method 524 - "Measurement of Purgeable Organic Compounds in Drinking Water by Gas Chromatography/Mass Spectrometry". |

[1]Additional information on this method is available from the Environmental Monitoring and Support Laboratory, 26 West St. Clair Street, Cincinnati, Ohio 45268.

cc: Robert L. Booth, Acting Director, EMSL
Ann Alford-Stevens, Chemist, EMSL
Regional Water Supply Representatives
Regional Quality Assurance Officers

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Method 524. Measurement of Purgeable Organic Compounds in Drinking Water By Gas Chromatography/Mass Spectrometry

## 1. SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for identification and measurement of purgeable organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that have sufficiently high volatility and low water solubility to be removed from water samples with purge and trap procedures. Single-laboratory method efficiency, accuracy and precision data have been determined for the following compounds:

| Analyte | Chemical Abstracts Service Registry Number (CASRN) | STORET Number |
|---|---|---|
| benzene | 71-43-2 | 34030 |
| bis(2-chloroisopropyl) ether | 39638-32-9 | 34283 |
| bromochloromethane | 74-97-5 | 77297 |
| bromodichloromethane | 75-27-4 | 32101 |
| 4-bromofluorobenzene | 460-00-4 | |
| bromoform | 75-25-2 | 32104 |
| carbon tetrachloride | 56-23-5 | 32102 |
| chlorobenzene | 108-90-7 | 34301 |
| chlorodibromomethane | 124-48-1 | 32105 |
| chloroform | 67-66-3 | 32106 |
| chloromethane | 74-87-3 | 34418 |
| 1,2-dibromo-3-chloropropane | 96-12-8 | |
| 1,2-dichlorobenzene | 95-50-1 | 34536 |
| 1,3-dichlorobenzene | 541-73-1 | 34566 |
| 1,2-dichloroethane | 107-06-2 | 34531 |
| 1,1-dichloroethene | 75-35-4 | 34501 |
| trans-1,2-dichloroethene | 156-60-5 | 34546 |
| cis-1,3-dichloropropene | 10061-01-5 | 34699 |
| methylene chloride | 75-09-2 | 34423 |
| styrene (ethenylbenzene) | 100-42-5 | 77128 |
| 1,1,2,2-tetrachloroethane | 79-34-5 | 34516 |
| tetrachloroethene | 127-18-4 | 34475 |
| toluene | 108-88-3 | 34010 |
| 1,1,1-trichloroethane | 71-55-6 | 34506 |
| 1,1,2-trichloroethane | 79-00-5 | 34511 |
| trichloroethene | 79-01-6 | 39180 |
| vinyl chloride | 75-01-4 | 30175 |
| p-xylene | 106-42-3 | |

A laboratory may use this method to detect and measure additional analytes after the laboratory obtains acceptable (defined in Section 10) accuracy and precision data for each added analyte.

1.2 Detection Limits (MDLs) (1) are compound dependent, varying with purging efficiency and concentration, where MDL is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero. For the listed analytes in reagent water, MDLs vary from 0.07 to 11.2 µg/L. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.2 µg to 200 µg of analyte per liter of undiluted sample. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

1.3 Determination of some individual components of complex mixtures may be hampered by insufficient chromatographic resolution and/or by large differences in concentrations of individual components.

## 2. SUMMARY OF METHOD

Highly volatile organic compounds with low water solubility are removed (purged) from the sample matrix by bubbling helium through a 25-mL aqueous sample. Purged sample components are trapped in a stainless steel tube containing suitable sorbent materials. 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). Compounds eluting from the GC column are tentatively identified by comparing their mass spectra to reference spectra in a data base. Tentative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is measured by relating the MS response for an appropriate selected ion produced by that compound to the MS response for the same ion from that same compound in an external standard or for another ion produced by a compound that is used as an internal standard.

## 3. DEFINITIONS

External standard -- 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.

Internal standard -- 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 a sample component.

Field duplicates -- two samples taken at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Field reagent blank -- reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures.

Laboratory control standard -- a solution of analytes prepared in the laboratory by dissolving known amounts of pure compounds in a known amount of reagent water. In this method, the laboratory control standard is prepared by adding appropriate volumes of the secondary dilution standard solution and the internal standard/surrogate compound spiking solution to reagent water.

Laboratory duplicates -- two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation or storage procedures.

Laboratory reagent blank -- a 25-mL portion of reagent water placed in the purging apparatus and analyzed as if it were a sample.

Performance evaluation sample -- a methanol solution of method analytes distributed by the Quality Assurance Branch (QAB), Environmental Monitoring and Support Laboratory, USEPA, Cincinnati, Ohio, to multiple laboratories for analysis. A small volume of the methanol solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by the QAB to determine statistically the accuracy and precision that can be expected when a method is performed by competent analysts. Analyte true values are unknown to the analyst.

Quality control check sample -- a methanol solution containing known concentrations of analytes prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method. A small volume of the methanol solution is added to a known volume of reagent water and analyzed with procedures used for samples. True values of analytes are known by the analyst.

Secondary dilution standard -- a methanol solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare aqueous calibration solutions and laboratory control standards.

Stock standard solution -- a concentrated solution containing a certified standard that is a method analyte, or a concentrated methanol solution of an analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare secondary standard solutions.

Surrogate compound -- a compound that is not expected to be found in the sample, is added to the original environmental sample to monitor performance, and is measured with the same procedures used to measure sample components.

## 4. INTERFERENCES

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

4.2 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. Analyses of field reagent blanks and laboratory reagent blanks provide information about the presence of contaminants.

4.3 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. 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 volatile organic compounds, the system should be baked for 10 min by passing helium through the sample purging chamber into the heated (180°) sorbent trap. One or more laboratory reagent blanks should be analyzed to ensure that accurate values are obtained for the next sample.

## 5. SAFETY

5.1 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 (2-4).

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

## 6. APPARATUS AND EQUIPMENT

6.1 Sample containers -- 120-mL or larger glass bottles each equipped with a screw cap and a polytetrafluoroethylene-faced silicone septum.

6.2 Purge and trap device consisting of sample purging chamber, sorbent trap and desorber. (Acceptable devices are commercially available.)

6.2.1 The all glass sample purging chamber holds 25-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 ≤5 mm from the base of the water column.

6.2.2 The stainless steel sorbent trap is 25 cm long by 2.5 mm ID and is packed with 8 cm of Tenax-GC$^R$, 8 cm of silica gel, and 8 cm of charcoal, in that order with respect to the inlet end of the trap. The charcoal is not necessary for listed analytes but is necessary if fluorine-substituted methanes and ethanes (fluorocarbons) are among additional analytes. When analytes do not include fluorocarbons, the charcoal may be eliminated, and the amount of Tenax-GC$^R$ may be increased. A trap with different dimensions can be used if it has been evaluated and found to perform satisfactorily (i.e., provides method efficiencies equal to or better than those in Table 2). 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.

6.2.3 The desorber should be capable of rapidly heating the trap to 180°C. The trap section containing Tenax-GC$^R$ should not be heated to higher than 180°C, and the temperature of the other sections should not exceed 200°C.

6.3 SYRINGES AND SYRINGE VALVES

6.3.1 Two 25-mL glass hypodermic syringes with Luer-Lok$^R$ tip (if applicable to the purging device being used).

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

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

6.3.4 Micro syringes, various sizes.

6.4 MISCELLANEOUS

6.4.1 Standard solution storage containers -- 10-mL bottles with polytetrafluoroethylene-lined screw caps.

6.4.2 Analytical balance capable of weighing 0.0001 g accurately.

6.4.3 Helium purge gas, as contaminant free as possible.

6.5 GAS CHROMATOGRAPH/MASS SPECTROMETER/DATA SYSTEM (GC/MS/DS)

6.5.1 The GC must be capable of temperature programming. Any column (either packed or capillary) that provides data with adequate accuracy and precision (Sect. 10) can be used. If a packed column is used, the GC usually is interfaced to the MS with an all-glass enrichment device and an all-glass

transfer line, but any enrichment device or transfer line can be used if performance specifications described in this method can be demonstrated with it. If a capillary column is used, an enrichment device is not needed. A recommended packed GC column for the listed analytes is 1.8 m long by 2 mm ID glass packed with 1% SP-1000 on 60/80 mesh Carbopack B. Recommended operating parameters for that column are: helium carrier gas flow rate of 30 mL/min and temperature of 45°C for 4 min, increased to 230°C at a rate of 8°C/min, and isothermal at 230°C for at least 25 min or until all expected analytes elute. An alternative recommended packed 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.

6.5.2 Mass spectral data are obtained with electron-impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 450 amu every 7 s or less and 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. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC. With capillary columns which produce narrower peaks than packed columns that criterion may not be feasible and adequate precision with fewer spectra per GC peak must be demonstrated (Sect. 10).

6.5.3 An interfaced data system (DS) is required to acquire, store, reduce and output mass spectral data. The computer software must allow searching any GC/MS data file for ions of a specific mass and plotting ion abundances versus time or scan number. This type of plot is defined as an extracted ion current profile (EICP). Software must also allow integrating the abundance in any EICP between specified time or scan number limits.

## 7. REAGENTS AND CONSUMABLE MATERIALS

### 7.1 SORBENT TRAP PACKING MATERIALS

7.1.1 Polymer based on 2,6-diphenyl-p-phenylene oxide -- 60/80 mesh Tenax-GC$^R$, chromatographic grade, or equivalent.

7.1.2 Coconut charcoal -- 26 mesh.

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

### 7.2 REAGENTS

7.2.1 Methanol -- pesticide quality or equivalent.

7.2.2 Reagent water -- water in which an interferent is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, 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. Store in clean, narrow-mouth bottles with polytetrafluoroethylene-lined septa and screw caps.

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

7.3 STOCK STANDARD SOLUTIONS -- These solutions may be purchased as certified solutions or prepared from pure standard materials using the following procedures:

7.3.1 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.

7.3.2 If the analyte is a liquid at room temperature, with a 100-µL 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). If the analyte is a gas at room temperature, fill a 5-mL valved gas-tight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck of the flask. (The gas will rapidly dissolve in the methanol.)

7.3.3 Reweigh the flask, dilute to volume, stopper, and mix by inverting several times.

7.3.4 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.

7.3.5 Store stock standard solutions with minimal headspace in polytetrafluoroethylene-lined screw-capped bottles. Methanol solutions of listed liquid analytes are stable for at least four weeks when stored at 4°C. Methanol solutions prepared from listed gaseous analytes are not stable for more than one week when stored at <0°C; at room temperature, they must be discarded after one day.

7.4 SECONDARY DILUTION STANDARD -- Use stock standard solutions to prepare a secondary dilution standard solution that contains the analytes in methanol. The secondary dilution standard should be prepared at a concentration that can be easily diluted to prepare

aqueous calibration solutions (Section 9.2.1.2) at concentrations that will bracket the working concentration range. Store the secondary dilution standard solution with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions from it.

7.5 INTERNAL STANDARD SPIKING SOLUTION AND SURROGATE COMPOUND SPIKING SOLUTION -- Prepare a solution of fluorobenzene in methanol at a concentration that allows use of 2 to 10 µL to add an appropriate amount of fluorobenzene to each sample; this amount should be approximately the same as the amount of the analyte to be measured. 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 performance. Fluorobenzene was selected because it is stable in aqueous solutions, is efficiently purged, does not occur naturally, and is not commercially produced in bulk quantities but is available as a laboratory reagent chemical.

## 8. SAMPLE COLLECTION, PRESERVATION AND HANDLING

8.1 Collect all samples in duplicate. Fill sample bottles 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. Keep samples sealed from collection time until analysis. Maximum storage times vary with analytes of concern. Recent studies (5-6) provided data indicating appropriate storage times for samples (river and drinking water) containing compounds that are potential method analytes (Tables 3 and 4).

8.1.1 When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 min). Adjust the flow to about 500 mL/min and collect duplicate samples from the flowing stream.

8.1.2 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.

8.2 SAMPLE PRESERVATION

8.2.1 If styrene (which reacts with chlorine) and/or trihalomethanes are to be measured in a sample expected to contain residual chlorine, add a reducing agent, sodium thiosulfate or sodium sulfite (30 mg per 120-mL sample for up to 5 ppm chlorine) to the empty sample bottle before it is shipped to the sampling site.

NOTE: Some possible analytes may be unstable in the presence of reducing agent. Data (5) indicate that sodium sulfite should not be used if analytes include chloromethane, 1,1-dichloroethene, 1,1-dichloropropene,

2-chloroethyl ethyl ether, or 1,1,2,2-tetrachloroethane; sodium thiosulfate is not recommended if analytes include chloromethane or 1,2-dibromoethane.

8.2.2 Much remains to be learned about biological degradation of aromatic hydrocarbon analytes. Currently, two preservation techniques are recommended but both have negative aspects.

8.2.2.1 Hydrochloric acid may be used at the sampling site to adjust the sample pH to < 2; the major disadvantages of this procedure are that shipping acid is restricted by federal regulations and that effects of low pH on other analytes (such as organohalides) are largely unknown.

8.2.2.2 Mercuric chloride may be added to the sample bottle in amounts to produce a concentration of 10 mg/L. This may be added to the sample at the sampling site or to the sample bottle in the laboratory before shipping to the sampling site. A major disadvantage of mercuric chloride is that it is a highly toxic chemical; it must be handled with caution, and samples containing it must be disposed with appropriate procedures.

8.2.2.3 If analytes include both aromatic hydrocarbons and styrene or trihalomethanes, current recommendations are either to add both preservative types (reducing agent along with acid or mercuric chloride) or to collect two samples with the appropriate preservative type in each.

8.2.3 After addition of preservative(s), seal the sample bottle and shake vigorously for 1 min.

8.3 FIELD BLANKS

8.3.1 Duplicate field reagent blanks must be handled along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill field blank sample bottles with reagent water, seal, and ship to the sampling site along with empty sample bottles and back to the laboratory with filled sample bottles. Wherever a set of samples is shipped and stored, it is accompanied by appropriate blanks.

8.3.2 When reducing agent or preservative(s) is added to samples, use the same procedures used for samples to add the same amount to blanks. The reducing agent can be added in the laboratory.

# 9. CALIBRATION

## 9.1 INITIAL CALIBRATION

### 9.1.1 CALIBRATION SOLUTIONS

9.1.1.1 At least three calibration solutions, each containing a standard of each analyte, are needed. (More than three calibration solutions may be required if analytes are numerous.) One calibration solution should contain each analyte at a concentration approaching but greater than the method detection limit (Table 5) for that compound; the other two solutions should contain analytes at concentrations that bracket the range expected in samples. For example, if the detection limit for a particular analyte is 0.2 µg/L, and a 25-mL sample expected to contain approximately 5 µg/L is analyzed, aqueous solutions of standards should be prepared at concentrations of 0.3 µg/L, 5 µg/L, and 10 µg/L.

9.1.1.2 To prepare calibration solutions, add appropriate volumes (µL) of the secondary dilution standard solution to aliquots of reagent water. Remove the plunger from a 25-mL syringe and attach a closed syringe valve. Fill the syringe with reagent water, replace the plunger, and compress the water. Open the syringe valve and vent air. Adjust the reagent water volume to 25 mL and add a carefully measured aliquot of 2.0 to 18.0 µL of the secondary dilution standard through the valve bore. Add the appropriate amount ($\geq$ 2.0 µL) of the internal standard surrogate spiking solution through the valve bore, but do not add more than 20 µL total volume of methanol solution.

NOTE: If appropriate concentrations cannot be prepared without adding more than 20 µL of the secondary dilution standard to 25 mL of reagent water, prepare a new secondary dilution standard. If less than 2.0 µL must be added to obtain appropriate concentrations, prepare a larger volume of the calibration solution in a volumetric flask. Mix by inverting the flask several times, and transfer a 25-mL portion into the sample syringe. The remaining solution may be stored in screwcap vials with no headspace. If aromatic compounds are among calibration solution components, do not store for more than

1 h. Other aqueous solutions can be stored for up to 24 h.

9.1.2 Analyze triplicate aliquots of each calibration solution with the procedures to be used to analyze samples.

9.1.2.1 If the external standard technique is being used, prepare a concentration calibration curve for each analyte by plotting integrated abundances of the ion characteristic of that compound as a function of the concentration. If the ratio of ion abundance to amount of analyte is constant (< 10% relative standard deviation) throughout the concentration range, the average ratio may be used instead of a calibration curve.

9.1.2.2 If the internal standard technique is being used, calculate the mass spectrometer response to each compound relative to fluorobenzene, the internal standard. Calculate the response factor (RF) with the equation,

$$RF = \frac{A_x \cdot Q_s}{A_s \cdot Q_x},$$

where $A_x$ = integrated abundance of the selected ion for the analyte standard;
$A_s$ = integrated abundance of the selected ion for the internal standard;
$Q_s$ = quantity of internal standard; and
$Q_x$ = quantity of analyte standard.

RF is a unitless number; units used to express quantities of analyte and internal standard must be equivalent. Ideally, the response factor for each analyte should be independent of analyte quantity for the working range of the calibration, but required linearity will vary with required accuracy of analyte concentration measurements. Generally, acceptable variations of mean RF values are ± 15% over a concentration range of two orders of magnitude and ± 10% RSD of values obtained from analyses of triplicate aliquots of each concentration calibration solution. For an analyte with non-linear RF, a calibration curve of $Area_x/Area_s$ plotted versus $Q_x$ may be used to determine an analyte concentration.

9.2 DAILY CALIBRATION -- Check calibration data each day by measurement of one or more laboratory control standards or calibration solutions. If the expected ion abundance was observed (Sect. 10.5) for 50 ng of the MS performance standard but the absolute ion abundance

measured for any analyte varies from expected abundance by more than 15%, prepare and analyze a fresh calibration solution to determine if the problem is being caused by deterioration of the calibration solution or by a malfunction in the purge and trap apparatus. When the internal standard technique is being used, verify each day that response factors have not changed. When changes occur (> 10% relative standard deviation), prepare and analyze new standard solutions to determine new response factors.

NOTE: Some analysts have observed marked deterioration of MS response after the initial purge and trap analysis each day; if this phenomenon is observed, perform one purge/desorb cycle before checking MS performance and calibration data.

## 10. QUALITY CONTROL

10.1 Minimum quality control requirements consist of:

10.1.1 initial demonstration of laboratory analytical capability (efficiency, accuracy and precision procedures, Sect. 10),

10.1.2 analysis of an MS performance standard and a laboratory control standard near the beginning of each 8-h work period,

10.1.3 analysis of a field reagent blank along with each sample set,

10.1.4 analysis of a laboratory reagent blank when the field reagent blank contains analytes at concentrations above the method detection limits,

10.1.5 quarterly analysis of a quality control check sample, (if available for analytes of concern), and

10.1.6 continued maintenance of performance records to define the quality of generated data.

10.2 METHOD EFFICIENCY -- For each analyte, calculate method efficiency 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 low method efficiency may cause unacceptably high detection limits. Measure method efficiency for each analyte whenever the analytical system undergoes major modification, such as replacement of trap packing.

10.2.1 Analyze at least five laboratory control standards with the purge, trap, desorption and GC/MS detection procedures. Interspersed among these five or more analyses, inject two or more aliquots of the secondary dilution standard solution

(Section 7.4) directly into the GC to introduce each analyte in an amount equal to that introduced by purge and trap procedures. Use the same MS data acquisition parameters for injected analytes as those used for purge and trap procedures.

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

$$E = \frac{A_p}{A_i} \cdot 100 \quad ,$$

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.

10.2.3 Calculate the mean method efficiency for each analyte. Acceptable detection limits usually can be achieved even if the mean method efficiency is only 20 to 30%.

10.3 ACCURACY -- To determine accuracy, analyze duplicate aliquots of a quality control (QC) check sample containing known amounts of analytes of concern. QC check samples for some, but not all listed analytes, currently are available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio 45268; alternatively certified standard solutions may be purchased from commercial vendors.

10.3.1 When using the external standard procedure, calculate accuracy as the ion abundance found in the QC sample solution expressed as a percentage (P) of the ion abundance found in the external standard solution:

$$P = \frac{A_x}{A_s} \cdot 100 \quad ,$$

where $A_x$ = abundance of ion used to measure an analyte in an aliquot of the QC check sample, and
$A_s$ = abundance of ion used to measure an equal amount of the same analyte treated as an external standard.

10.3.2 When using the internal standard procedure, fluorobenzene in the solution of analyte standards is the internal standard.

Calculate response factors (Sect. 9.3.4) for each analyte relative to fluorobenzene. With these response factors, calculate accuracy with data acquired for the QC check sample:

$$P = \frac{A_x \cdot 100}{A_s \cdot RF} ,$$

where $A_x$ = abundance of ion used to measure an analyte in an aliquot of the QC check sample,
$A_s$ = abundance of ion used to measure fluorobenzene in the same aliquot, and
RF = response factor of the particular analyte relative to fluorobenzene.

NOTE: The internal standard concentration is constant in calibration solutions and all samples for which the calibration solutions are used (Section 9.3).

10.3.3 For each analyte, the mean accuracy should be in the range of 85 to 115%. For some listed analytes, this may not be feasible for low concentration measurements.

10.4 PRECISION

10.4.1 For each analyte, calculate method precision as the standard deviation (s, in µg/L) of the replicate measured values obtained in the accuracy calculations:

$$s = \frac{n \sum_{i=1}^{n} X_i^2 - \sum_{i=1}^{n} X_i^2}{n(n-1)} ,$$

where n = number of measurements for each analyte, and
X = individual measured value.

10.4.2 For the set of measured values for each analyte, calculate the dispersion as the percent relative standard deviation (RSD):

$$RSD = \frac{s}{\bar{C}} \cdot 100 ,$$

where s = standard deviation, and
C = mean observed concentration.

10.4.3 Adequate precision is obtained when the relative standard deviation is $\leq$ 20%. For some listed analytes, this may not be feasible for low concentration measurements.

10.5 MS PERFORMANCE STANDARD

10.5.1 Near the beginning of each 8-h work period in which analytes are to be measured, measure the mass spectrum produced by 50 ng of p-bromofluorobenzene (BFB) 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. It may be a component of the laboratory control standard analyzed daily to check calibration (Sect. 7). Measure the entire mass spectrum at an MS scan rate that produces at least five spectra for the BFB GC peak but does not exceed 7 s per spectrum. Although acquisition of five spectra per BFB GC peak may not be feasible when capillary columns are used, BFB performance criteria still must be met. If the BFB spectrum is unacceptable, adjust GC/MS operating parameters until an acceptable spectrum is produced before samples are analyzed.

10.5.2 Record the absolute ion abundance detected for 50 ng of BFB. If ion abundance varies more than ± 10% from the expected number, check the GC/MS system to locate and correct the problem. Preparation of a new calibration curve may be necessary if the system is operating acceptably but with decreased sensitivity.

10.6 LABORATORY CONTROL STANDARD -- To demonstrate that the calibration curve is still valid, analyze a laboratory control standard at the beginning of each 8-h work period.

10.6.1 For each analyte to be measured, select a concentration representative of its occurrence in drinking water samples.

10.6.2 Prepare the laboratory control standard with either of the following procedures:

10.6.2.1 From stock standard solutions, prepare a laboratory control standard concentrate in methanol. This solution should contain analytes at concentrations 2500 times those selected as representative concentrations. Add 10 µL of the laboratory control standard concentrate to a 25-mL aliquot of reagent water.

10.6.2.2 Add 2 to 18 µL of the secondary dilution standard to 25 mL of reagent water contained in the sample syringe.

10.6.3 Add an appropriate volume of the internal standard/surrogate spiking solution and analyze with the same procedures (Sect. 11) to be used for samples.

10.6.4 Determine calibration acceptability and appropriate remedial actions, if needed. (For the external standard technique, see Sect. 9.1.2.1; for the internal standard technique, see Sect. 9.1.2.2.)

10.7 MONITORING THE SURROGATE COMPOUND/INTERNAL STANDARD -- Because all samples and laboratory control standards contain equal amounts of the internal standard/surrogate compound, use the absolute ion abundance for the characteristic ion of that compound, fluorobenzene, to monitor system performance. If for any sample, the absolute ion abundance varies more than 15% from that observed in the previous sample or laboratory control standard, do not report analyte values obtained for that sample, and take remedial actions to solve the system performance problem.

10.8 FIELD REAGENT BLANKS -- Analyze a field reagent blank along with each sample set. If a field reagent blank contains analytes at concentrations above the method detection limits, analyze a laboratory reagent blank. If one or more analytes that are not detected at concentrations above method detection limits in the laboratory reagent blank are detected in significant amounts in the field blank, sampling or storage procedures have not prevented sample contamination, and the appropriate analyte measurement(s) must be discarded.

10.9 At least quarterly, analyze a quality control check sample obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Quality Assurance Branch, Cincinnati, Ohio. Quality control check samples currently are available for some but not all listed analytes. If measured analyte concentrations are not within ±20% of true values, check the entire analytical procedure to locate and correct the problem source.

10.10 Additional QC procedures may be necessary, depending on the purpose of the analysis performed with this method.

10.10.1 Laboratory Duplicates -- To determine precision associated with laboratory techniques, analyze two aliquots (Sect. 11.1.2) of a sample in which some analytes were detected in measurable quantities. Calculate the range (R) of concentrations measured for each duplicate pair:

$$R = C_1 - C_2,$$

where $C_1$ represents the larger and,
$C_2$ represents the smaller of the two measurements.

Calculate percent relative range (RR) of duplicate analyses using the formula:

$$RR = \frac{R}{\bar{C}} \cdot 100 \quad ,$$

where R = range of concentrations measured, and
C = mean concentration measured.
Generally, if RR is greater than 30%, precision is inadequate, and laboratory techniques must be improved.

10.10.2 Field Duplicates -- Analyze 10% of samples in which some analytes were detected in measurable quantities to indicate precision limitations imposed by sampling, transport and storage techniques as well as laboratory techniques. If acceptable results are obtained from analysis of field duplicates, analysis of laboratory duplicates is usually not necessary.

10.10.3 Matrix Effects Determination -- To indicate matrix effects on method efficiency, accuracy and precision when raw source waters or drinking water during treatment is to be analyzed, analyze aliquots to which known amounts of analytes have been added. Because analytes may be present in the unspiked aliquots, analysis of one or more unspiked aliquots is necessary to determine initial concentrations, which are then subtracted from concentrations measured in spiked aliquots. For each analyte the amount added to determine matrix effects should exceed twice the amount measured in unspiked aliquots.

## 11. PROCEDURE

### 11.1 ANALYSIS PROCEDURES

11.1.1 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.

11.1.2 Sample introduction and purging -- Remove the plunger from a 25-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 25.0 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 2 to 20 µL of the spiking solution (Sect. 7.5) 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. Because temperature affects purging efficiencies of some analytes, purging chamber temperature must be controlled to maintain constant (approximately ± 2°C) temperature throughout calibration and sample analyses. If laboratory temperature is not controlled adequately, the purging chamber can be placed in a thermostatically controlled water bath.

11.1.3 Desorption and data acquisition -- At the conclusion of purging, adjust the purge and trap apparatus to the desorb mode, and initiate GC temperature programming, trap heating, and MS data acquisition. Desorb for 4 min. Transfer trapped sample components into the GC column by heating the trap to 180°C rapidly while it is backflushed with helium flowing at 20 to 60 mL/min. (If the trap cannot be heated rapidly, use the GC column as a secondary trap by cooling the column to < 30°C during desorption.)

11.1.4 Sample chamber rinsing -- During or after desorption empty the purging chamber with the sample introduction syringe, and rinse the chamber with two 25-mL portions of reagent water.

11.1.5 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 (<25°C), the trap is ready for the next sample.

11.1.6 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 full range mass spectra and appropriate extracted ion current profiles (EICPs). 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.

11.2 IDENTIFICATION PROCEDURES CRITERIA -- Tentatively identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in a collection. Use the following criteria to confirm a tentative identification:

11.2.1 The GC retention time of the sample component must be within $\underline{t}$ s of the time observed for that same compound when a calibration solution was analyzed. Calculate the value of $\underline{t}$ with the equation:

$$\underline{t} = (RT)^{1/3}$$

where RT = observed retention time (in seconds) of the compound when a calibration solution was analyzed.

11.2.2 All ions that are present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample component and should agree within absolute 10%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 20 to 40%.

11.2.3 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining EICPs of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria described in Section 11.2.2 can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.2.4 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

## 12. CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations, if unique ions with adequate intensities are selected for EICPs. For example, although two listed analytes, 1,1,2,2-tetrachloroethane and tetrachloroethene, were not resolved with the GC conditions used and produced mass spectra containing common ions, concentrations (Table 5) were calculated by measuring appropriate characteristic ions.

12.1.1 With either the internal or external standard technique, calculate analyte concentrations with the equation:

$$C_x = \frac{A_x \cdot Q_s}{A_s \cdot RF \cdot V} ,$$

where $C_x$ = analyte concentration in micrograms per liter;
$A_x$ = integrated ion abundance of a significant characteristic ion of the sample analyte;
$A_s$ = integrated ion abundance of a significant 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 quantity of external standard that produced $A_s$, in micrograms; and
V = purged sample volume in liters.

12.1.2 With the external standard technique, $A_s$ is a point on the concentration calibration curve and is the same number as $A_x$; $Q_s$ is the quantity that produces $A_s$ and also is obtained from the concentration calibration curve.

12.1.3 For each analyte, select a significant characteristic ion. When feasible, use the most intense ion in the mass spectrum; when a less intense ion is more characteristic and sufficiently intense to provide necessary sensitivity, use that ion to avoid possible interferences.

## 13. PRECISION AND ACCURACY

13.1 To obtain method efficiency data (Table 2) and to indicate anticipated single laboratory accuracy and precision data (Table 5) for each listed analyte, seven 25-mL aliquots of each of two solutions of reagent water containing known amounts of analytes were analyzed with purge and trap procedures and a packed column. One solution contained 16 µg of analyte per liter of solution; the other contained 1.6 µg/L. Two direct injections of appropriate volumes of secondary dilution standard were interspersed among purged aliquots. To obtain the data in Table 5, one aliquot of each of the two laboratory control standards was randomly selected to be a solution with known true values of analytes. This aliquot was treated as an external standard, and the other six aliquots of each of the two solutions were treated as samples.

13.1.1 Except for two listed analytes, mean method efficiency varied among analytes from 25.0% to 118.7%. Those two analytes, 1,2-dibromo-3-chloropropane and bis(2-chloroisopropyl) ether, are very inefficiently purged and were not detected in aliquots containing 1.6 µg/L; mean method efficiencies for these two analytes when purged from 16 µg/L aliquots were 9.4% and 4.3%, respectively (Table 2). Although for some applications these low efficiencies may result in unacceptably high detection limits for those

analytes, they can be measured with acceptable accuracy and precision when present at a concentration of 16 µg/L (Table 5).

13.1.2 With these data, MDLs were calculated using the formula:

$$MDL = t_{(n-1,1- \ = 0.99)} \quad s,$$

where:

$t_{(n-1,\ 1- \ = 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom, where n - number of replicates, and

s = standard deviation of replicate analyses.

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Table 2. Single Laboratory Method Efficiency Data[a] for Purgeable Organic Compounds Measured with GC/MS

| Compound | Measured Ion | Rel. Ret. Time[b] | True Conc. µg/L | Mean Method Efficiency % | Rel. Std. Dev., % |
|---|---|---|---|---|---|
| chloromethane | 50 | 0.10 | 1.6 | | |
| | | | 16 | 108.5 | 15.2 |
| vinyl chloride | 62 | 0.14 | 1.6 | | |
| | | | 16 | 53.8 | 13.6 |
| methylene chloride | 84 | 0.22 | 1.6 | 118.7 | 4.9 |
| | | | 16 | 81.9 | 7.6 |
| 1,1-dichloroethene | 96 | 0.28 | 1.6 | 93.8 | 5.1 |
| | | | 16 | 88.1 | 7.9 |
| bromochloromethane | 128 | 0.30 | 1.6 | 68.8 | 5.8 |
| | | | 16 | 65.0 | 6.2 |
| trans-1,2-dichloroethene | 96 | 0.31 | 1.6 | 50.0[c] | 30.5[c] |
| | | | 16 | 98.8[c] | 12.6[c] |
| chloroform | 83 | 0.44 | 1.6 | 93.8 | 3.8 |
| | | | 16 | 92.5 | 2.1 |
| 1,2-dichloroethane | 62 | 0.50 | 1.6 | 62.5 | 12.6 |
| | | | 16 | 55.6 | 7.1 |
| 1,1,1-trichloroethane | 97 | 0.59 | 1.6 | 93.8 | 3.8 |
| | | | 16 | 90.6 | 2.9 |
| carbon tetrachloride | 117 | 0.62 | 1.6 | 106.2 | 2.2 |
| | | | 16 | 110.0 | 1.9 |
| bromodichloromethane | 83 | 0.66 | 1.6 | 81.3 | 5.9 |
| | | | 16 | 80.6 | 5.4 |
| 1,1,2-trichloroethane | 97 | 0.79 | 1.6 | 18.8[c] | 33.5[c] |
| | | | 16 | 50.0[c] | 15.9[c] |
| trichloroethene | 130 | 0.84 | 1.6 | 100.0 | 3.0 |
| | | | 16 | 106.9 | 1.2 |
| benzene | 78 | 0.88 | 1.6 | 106.2 | 2.9 |
| | | | 16 | 96.3 | 2.2 |
| chlorodibromomethane | 129 | 0.88 | 1.6 | 58.8 | 6.0 |
| | | | 16 | 53.8 | 11.3 |
| cis-1,3-dichloropropene | 75 | 0.90 | 1.6 | 25.0[c] | 31.6[c] |
| | | | 16 | 70.0[c] | 11.8[c] |
| fluorobenzene | 96 | 1.00 | 1.6 | 100.0 | 7.4 |
| | | | 16 | 95.6 | 11.1 |

Table 2. (continued)

| Compound | Measured Ion | Rel. Ret. Time[b] | True Conc. µg/L | Mean Method Efficiency % | Rel. Std. Dev., % |
|---|---|---|---|---|---|
| bromoform | 173 | 1.10 | 1.6 | 39.4 | 7.0 |
| | | | 16 | 35.0 | 6.3 |
| 1,1,2,2-tetrachloroethane | 83 | 1.29 | 1.6 | 28.1 | 5.9 |
| | | | 16 | 25.0 | 6.3 |
| tetrachloroethene | 164 | 1.31 | 1.6 | 106.2 | 0.0 |
| | | | 16 | 107.5 | 4.6 |
| toluene | 92 | 1.42 | 1.6 | 100.0 | 3.2 |
| | | | 16 | 102.5 | 1.5 |
| chlorobenzene | 112 | 1.52 | 1.6 | 93.8 | 3.5 |
| | | | 16 | 96.3 | 2.2 |
| 1,2-dibromo-3-chloropropane[d] | 157 | 1.70 | 1.6 | --[d] | --[d] |
| | | | 16 | 9.4[c] | 10.3[c] |
| 4-bromofluorobenzene | 174 | 1.82 | 1.6 | 93.8 | 5.4 |
| | | | 16 | 93.8 | 4.0 |
| styrene | 104 | 1.93 | 1.6 | 68.8[c] | 29.2[c] |
| | | | 16 | 86.9[c] | 13.3[c] |
| p-xylene | 106 | 1.97 | 1.6 | 100.0 | 3.0 |
| | | | 16 | 103.1 | 1.5 |
| bis(2-chloroisopropyl) ether[d] | 45 | 2.08 | | | |
| | | | 16 | 4.3 | 14.3 |
| 1,3-dichlorobenzene | 146 | 2.19 | 1.6 | 75.0[c] | 28.3[c] |
| | | | 16 | 82.5[c] | 10.3[c] |
| 1,2-dichlorobenzene | 146 | 2.20 | 1.6 | 81.3 | 5.9 |
| | | | 16 | 79.4 | 4.2 |

[a] Except as noted, data were produced by purging seven aliquots of reagent water spiked with known amounts of listed compounds; calculations involved two direct injections.

[b] GC column: 1.8 m x 2 mm ID glass packed with 1% SP-1000 on 60/80 mesh carbopack B. Program: 45°C for 4 min; 8°C/min to 230°C. Retention time relative to fluorobenzene, which has retention time of 11.1 min under described GC conditions.

[c] Produced by analysis of six aliquots rather than seven.

[d] Compound is very inefficiently purged from water and was not detected in aliquots of 1.6 µg/L solution.

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 |

Table 3 (continued)

| Analyte | Demonstrated Acceptable Storage Time, Days |
|---|---|
| 2-chloroethylethyl ether | 27 |
| 2-chloroethylvinyl ether | 27 |
| bis-2-chloroethyl ether | 9[b] |
| bis-2-chloroisopropyl ether | 27 |

[a] These data were obtained by multiple analyses of raw river water and carbon-filtered chlorinated tap water to which known amounts (0.20 to 0.50 µg/L) of listed analytes had been added. Some samples were stored and analyzed periodically over a 21-day period; others, over a 27-day period. Data from "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," Method 502.1, EPA 600/4-81-059, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1981.

[b] Because of observed changes during storage, this number is the maximum recommended storage time.

Table 3. Acceptable Storage Times[a] for River and Drinking Water Samples Containing Halogenated Aliphatic Analytes

| Analyte | Demonstrated Acceptable Storage Time, Days |
|---|---|
| chloromethane | 21 |
| dichloromethane | 27 |
| carbon tetrachloride | 27 |
| bromomethane | 2[b] |
| dibromomethane | 21 |
| bromoform | 27 |
| bromochloromethane | 21 |
| bromodichloromethane | 27 |
| chlorodibromomethane | 27 |
| dichlorodifluoromethane | 27 |
| fluorotrichloromethane | 27 |
| chloroethane | 21 |
| 1,1-dichloroethane | 27 |
| 1,2-dichloroethane | 27 |
| 1,1,1-trichloroethane | 21 |
| 1,1,2-trichloroethane | 27 |
| 1,1,1,2-tetrachloroethane | 21 |
| pentachloroethane | 27 |
| 1,2-dibromoethane | 21 |
| chloroethylene (vinyl chloride) | 6[b] |
| 1,1-dichloroethylene | 27 |
| cis + trans-1,2-dichloroethylene | 27 |
| cis-1,2-dichloroethylene | 21 |
| 1,1,2-trichloroethylene | 27 |
| 1,1,2,2-tetrachloroethylene | 27 |
| 1,2-dichloropropane | 21 |
| 1,3-dichloropropane | 21 |
| 1,2,3-trichloropropane | 21 |
| 3-chloroprop-1-ene (allyl chloride) | 2[b] |
| 1,1-dichloroprop-1-ene | 27 |
| 2,3-dichloroprop-1-ene | 6[b] |
| trans-1,3-dichloroprop-1-ene | 1[b] |
| cis-1,3-dichloroprop-1-ene | 1[b] |
| 1-chlorohexane | 1[b] |
| chlorocyclohexane | 27 |
| 1-chlorocyclohex-1-ene | 27 |

Table 4. Storage Time Data[a] for River and Drinking Water Samples Containing Aromatic Analytes

| Analyte | Percent Recovery From River Water on Day 1 | | Acceptable[c] Storage Time in Days | | Observed Average Decay Rate (%/Day) in |
|---|---|---|---|---|---|
| | Preserved[b] | Unpreserved | Drinking Water | Preserved River Water | Preserved River Water |
| benzene | 100 | 12 | 15 | 14 | |
| toluene | 98 | 8 | 15 | 14 | |
| ethylbenzene | 95 | 10 | 15 | -- | 1.4 |
| o-xylene | 95 | 12 | 15 | -- | 1.6 |
| m-xylene | 93 | 17 | 15 | -- | 1.6 |
| p-xylene | 88 | 12 | 15 | -- | 2.3 |
| ethenylbenzene (styrene) | 83 | 0 | 0[d] | -- | 4.2 |
| n-propylbenzene | 88 | 15 | 15 | -- | 2.2 |
| isopropylbenzene | 93 | 0 | 15 | -- | 1.5 |
| n-butylbenzene | 88 | 3 | 15[e] | -- | 3.2 |
| sec-butylbenzene | 88 | 10 | 15 | -- | 2.2 |
| ter-butylbenzene | 90 | 43 | 15 | -- | 10 |
| 1-methyl-4-isopropylbenzene | 88 | 34 | 6 | -- | 2.3 |
| 1,2,4-trimethylbenzene | 85 | 16 | 15[f] | -- | 3.0 |
| 1,3,5-trimethylbenzene | 88 | 5 | 28 | -- | 2.1 |
| chlorobenzene | 90 | 23 | 28 | 26 | |
| bromobenzene | 90 | 17 | 28 | 26 | |
| o-dichlorobenzene | 96 | 85 | 28 | 26 | |
| m-dichlorobenzene | 96 | 96 | 28 | 26 | |
| p-dichlorobenzene | 94 | 90 | 28 | 26 | |
| 1,2,3-trichlorobenzene | 86 | 97 | 28 | 26 | |
| 1,2,4-trichlorobenzene | 88 | 88 | 28 | 26 | |
| o-chlorotoluene | -- | -- | 21 | -- | |
| p-chlorotoluene | 90 | 45 | 13 | 26 | |
| α-trifluorotoluene | 84 | 74 | 28 | 26 | |

[a] Data from "The Determination of Aromatic Chemicals in Water by the Purge and Trap Method," Method 503.1, EPA 600/4-81-057, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, May 1980, and from "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method," Method 502.1, EPA 600/4-81-059, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, OH, April 1981.

[b] Preservation was accomplished by adjustment of sample pH to 2.

[c] Data were obtained by multiple analyses of carbon-filtered tap water and preserved river water to which known amounts (0.40 or 0.50 μg/L) of listed analytes had been added. Mean recovery of analyte was $\geq$ 80% except as noted.

[d] Styrene, which reacts with free chlorine was not detected in chlorinated drinking water.

[e] Mean recovery of 78%.

[f] Mean recovery of 75%.

Table 5. Anticipated Accuracy and Precision Data with Method (Single Laboratory and Single Operator)

| Compound | Measured Ion | Rel. Ret. Time[b] | True Conc. µg/L | Mean Observed Conc., µg/L | Std. Dev. µg/L | Rel. Std. Dev.,% | Mean Method Accuracy % | Method Detection Limit[c], µg/L |
|---|---|---|---|---|---|---|---|---|
| chloromethane | 50 | 0.10 | 0[e] | | | | | |
| | | | 16 | 16.5 | 2.7 | 16.6 | 103.1 | 9.2 |
| vinyl chloride | 62 | 0.14 | 0[e] | | | | | |
| | | | 16 | 18.2 | 2.5 | 13.9 | 113.8 | 8.5 |
| methylene chloride | 84 | 0.22 | 1.6 | 1.6 | 0.08 | 4.8 | 100 | 0.25 |
| | | | 16 | 15.8 | 0.3 | 2.1 | 98.8 | -- |
| 1,1-dichloroethene | 96 | 0.28 | 1.6 | 1.6 | 0.08 | 4.9 | 100 | 0.27 |
| | | | 16 | 16.3 | 1.8 | 10.8 | 101.9 | -- |
| bromochloromethane | 128 | 0.30 | 1.6 | 1.6 | 0.08 | 5.2 | 100 | 0.28 |
| | | | 16 | 15.6 | 1.4 | 9.2 | 97.5 | -- |
| trans-1,2-dichloroethene | 96 | 0.31 | 1.6 | 1.3 | 0.5 | 37.9 | 81.3 | 1.7 |
| | | | 16 | 15.4 | 2.2 | 14.5 | 96.3 | -- |
| chloroform | 83 | 0.44 | 1.6 | 1.6 | 0.06 | 3.8 | 100 | 0.20 |
| | | | 16 | 16.0 | 0.32 | 2.0 | 100 | -- |
| 1,2-dichloroethane | 62 | 0.50 | 1.6 | 1.6 | 0.1 | 6.7 | 100 | 0.35 |
| | | | 16 | 16.0 | 1.7 | 10.5 | 100 | -- |
| 1,1,1-trichloroethane | 97 | 0.59 | 1.6 | 1.6 | 0.04 | 2.4 | 100 | 0.13 |
| | | | 16 | 16.2 | 0.8 | 4.9 | 101.3 | -- |
| carbon tetrachloride | 117 | 0.62 | 1.6 | 1.6 | 0.04 | 2.3 | 100 | 0.13 |
| | | | 16 | 16.0 | 0.4 | 2.4 | 100 | -- |
| bromodichloromethane | 83 | 0.66 | 1.6 | 1.6 | 0.09 | 5.5 | 100 | 0.29 |
| | | | 16 | 15.8 | 0.5 | 3.2 | 98.8 | -- |
| 1,1,2-trichloroethane | 97 | 0.79 | 1.6 | 1.3 | 0.3 | 23.1 | 81.3 | 1.0 |
| | | | 16 | 15.9 | 2.5 | 15.9 | 99.4 | -- |
| trichloroethene | 130 | 0.84 | 1.6 | 1.6 | 0.05 | 3.3 | 100 | 0.18 |
| | | | 16 | 16.0 | 0.2 | 1.1 | 100 | -- |
| benzene | 78 | 0.88 | 1.6 | 1.6 | 0.06 | 4.0 | 100 | 0.21 |
| | | | 16 | 16.1 | 0.5 | 3.1 | 100.6 | -- |
| chlorodibromomethane | 129 | 0.88 | 1.6 | 1.6 | 0.1 | 6.5 | 100 | 0.34 |
| | | | 16 | 15.0 | 2.0 | 13.6 | 93.8 | -- |
| cis-1,3-dichloropropene | 75 | 0.90 | 1.6 | 1.3 | 0.5 | 36.9 | 81.3 | 1.8 |
| | | | 16 | 15.0 | 1.8 | 11.7 | 93.8 | -- |
| fluorobenzene | 96 | 1.00 | | | | | | |

Table 5. (continued)

| Compound | Measured Ion | Rel. Ret. Time[b] | True Conc. µg/L | Mean Observed Conc., µg/L | Std. Dev. µg/L | Rel. Std. Dev.,% | Mean Method Accuracy % | Method Detection Limit[c],µg/L |
|---|---|---|---|---|---|---|---|---|
| bromoform | 173 | 1.10 | 1.6 | 1.5 | 0.1 | 6.5 | 93.8 | 0.34 |
| | | | 16 | 15.5 | 2.0 | 12.7 | 96.9 | -- |
| 1,1,2,2-tetrachloroethane | 83 | 1.29 | 1.6 | 1.6 | 0.08 | 5.3 | 100 | 0.28 |
| | | | 16 | 15.5 | 1.8 | 11.5 | 96.9 | -- |
| tetrachloroethene | 164 | 1.31 | 1.6 | 1.6 | 0.02 | 1.3 | 100 | 0.07 |
| | | | 16 | 15.8 | 0.4 | 2.4 | 98.8 | -- |
| toluene | 92 | 1.42 | 1.6 | 1.6 | 0.02 | 1.4 | 100 | 0.08 |
| | | | 16 | 15.9 | 0.3 | 1.6 | 99.4 | -- |
| chlorobenzene | 112 | 1.52 | 1.6 | 1.6 | 0.03 | 1.6 | 100 | 0.09 |
| | | | 16 | 15.7 | 0.6 | 3.6 | 98.1 | -- |
| 1,2-dibromo-3-chloropropane[d] | 157 | 1.70 | 1.6 | --[d] | --[d] | --[d] | --[d] | --[d] |
| | | | 16 | 15.7 | 3.0 | 19.1 | 98.1 | 10.1[d] |
| 4-bromofluorobenzene | 174 | 1.82 | 1.6 | 1.5 | 0.09 | 5.6 | 93.8 | 0.29 |
| | | | 16 | 15.6 | 1.1 | 7.3 | 97.5 | -- |
| styrene | 104 | 1.93 | 1.6 | 1.2 | 0.3 | 29.0 | 75.0 | 1.3 |
| | | | 16 | 15.8 | 1.6 | 10.4 | 98.8 | -- |
| p-xylene | 106 | 1.97 | 1.6 | 1.6 | 0.05 | 3.4 | 100 | 0.18 |
| | | | 16 | 16.1 | 0.2 | 1.0 | 100.6 | -- |
| bis(2-chloroisopropyl) ether[d] | 45 | 2.08 | 1.6 | --[d] | --[d] | --[d] | --[d] | --[d] |
| | | | 16 | 15.1 | 2.3 | 15.1 | 94.4 | 8.6[d] |
| 1,3-dichlorobenzene | 146 | 2.19 | 1.6 | 1.2 | 0.3 | 28.0 | 75.0 | 1.3 |
| | | | 16 | 15.2 | 1.5 | 9.8 | 95.0 | - |
| 1,2-dichlorobenzene | 146 | 2.20 | 1.6 | 1.5 | 0.09 | 6.2 | 93.8 | 0.30 |
| | | | 16 | 15.7 | 1.3 | 8.3 | 98.1 | - |

[a] Produced by analysis of seven aliquots of reagent water spiked with known amounts of listed compounds; calculations based on external standard technique. Two aliquots were treated as standards; five aliquots were treated as samples.

[b] GC column: 1.8 m x 2 mm ID glass packed with 1% SP-1000 on 60/80 mesh Carbopack B. Retention times relative to fluorobenzene.

[c] Minimum concentration that can be measured with 99% confidence that reported value is greater than zero.[1]

[d] Compound is inefficiently purged and was not detected in 1.6 µg/L solution; MDL was calculated from analysis of 16 µg/L solution.

[e] Compound not analyzed at concentration of 1.6 µg/L.