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1. Title

Measurement of Volatile Organic Compounds in Drinking Water by Gas Chromatography/Mass Spectrometry Using EPA Method 524.2

2. References

EPA Method 524.2, Revision 4.1, 1995

EPA Technical Notes on Drinking Water Methods, EPA/600/R-194/173, October 1994.

3. Scope and Principle of the Analysis

This is a general purpose method for the identification and measurement of purgeable volatile organic compounds in finished drinking water, raw source water, or drinking water in any stage. The following compounds are determined using this method:

Analyte	Chemical Abstract Services Registry Number
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8

1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Analyte	**Chemical Abstract Services Registry Number**
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	159-59-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	590-20-7
1,1-Dichloropropene	563-58-6
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3
Hexane	110-54-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methyl tert butyl ether (MtBE)	1634-04-4
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2-Tetrachloroethane	79-34-5
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4

1,2,3-Trichloropropane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m+p-Xylene	108-38-3/106-42-3

The compound names in ***bold and italic print*** are regulated compounds and Trihalomethanes. The above list reflects TO12 test group. The procedure described in this SOP applies to the following test groups: TO12, TO17, TO2, TO3, and TO4. See Appendix A for each target compound list.

Volatile Organic compounds and surrogates with low water solubility are purged by bubbling helium through the aqueous sample and then trapped in a tube with sorbent material (trap). The trap is then heated and back flushed with helium to desorb the trapped sample components onto a capillary gas chromatography column interfaced to a mass spectrometer. The column is temperature programmed to separate the analytes, which are subsequently detected by a mass spectrometer detector. Compounds are identified by comparing their mass spectra and retention times to reference spectra and retention times in the database. The concentration of the identified compounds is calculated by measuring the area of the target ion relative to the response of the target ion of an internal standard that is added to the sample. Surrogates, whose concentrations are known, are added to the sample and measured relative to the internal standard.

The applicable concentration range of this method is primarily column and matrix dependent, currently 0.5 – 10 µg/L.

Analytes that are not separated chromatographically, but have different mass spectra and no-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample. Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mix or water sample unless they have different retention times. Co-eluting compounds with very similar mass spectra must be reported as an isomeric group or pair.

4. Interferences

Interferences in the method can be due to contaminants in glassware, carryover, water, and contamination during transport. The following procedures are implemented to minimize the risk of contamination.

4.1. Glassware Cleaning

Glassware is cleaned in the laboratory washroom by washroom staff. Glassware is washed per the procedure outlined in the Washroom SOP. Once dry, the washed glassware is then stored in a cabinet in the VOA lab.

4.2. Sample Vial Cleaning

Sample vials are cleaned in the laboratory washroom by washroom staff. Vials are washed per the procedure outlined in the Washroom SOP. Once cleaned, the vials are baked at a high temperature in the VOA lab for a duration of no less than 2 hours. They are then cooled and capped and stored in the VOA laboratory.

4.3. Carryover

Interfering contamination may occur when a sample of low concentration is analyzed immediately after a sample containing relatively high concentrations of compounds (carryover). When a sample of high concentration is analyzed, the next run or runs are highly scrutinized. If the same compounds are found in these runs as in the sample of high concentration, then the possibility of carryover is present. If a sample is suspected of being contaminated by carryover, it MUST be re-analyzed.

4.4. Water

Due to the purging process associated with this method, water can also be a source of interference. Because of the recent developments in the GC/MS instrumentation, analytes that are desorbed are more efficiently placed and transferred from the end of the column to the MS. The analytes of interest are more concentrated but so is the water vapor that comes over in the purging process. The problem this causes is a quenching of response over time in the MS detector. This problem can be minimized by analyzing samples with a desorb time of 3 minutes.

4.5. Analysis of Field Blanks

Field Blanks (FBs) are defined as reagent blanks that are taken into the field and analyzed in the same exact manner as samples. FBs are indicators of the presence of contaminants in the field, the laboratory environment, the glassware, or the apparatus. If there is any contamination (target analytes recovered) in the field blank that is also present in the sample, the sample is rejected and re-sampling must occur.

5. Safety Issues

MSDS sheets are on file in the laboratory for reference to any safety issues concerning the chemicals used in this method. The safety procedures set out in the DOH Laboratory Chemical Hygiene Plan and Safety Manual are adhered to when performing this method.

The toxicity or carcinogenicity of chemicals used in this method varies for each compound, however, each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized.

Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Avoid breathing vapors, and contact with skin and eyes. Stock standard solutions of these compounds should be handled in a fume hood with proper personal protective equipment.

6. Apparatus and Equipment

6.1. Sample Bottles

Grab Sample Vials - 40mL amber borosilicate screw cap vials equipped with Teflon-silicone septa-lined caps. Prior to use, bottles and caps are prepared as in Section 8.

6.2. Glassware and Apparatus

- 10, 50, 100, and 200mL volumetric flasks.
- Gas-tight Syringes: various sizes.
- Vials: same as sample bottles (I-Chem Cat. # T346-0040, 72 vials and caps per case).
- Micro reaction vessels: various sizes

6.3. Instrumentation

Agilent GC/MS system consisting of the following:

Agilent 6890N Series Gas Chromatograph with Electronic Pressure Control Dual Split/Splitless Injector Port and direct capillary interface with Agilent 5973N Mass Selective Detector.

Purge and Trap- Tekmar Velocity XPT Purge and Trap Sample Concentrator or Tekmar Stratum Purge and Trap Sample Concentrator, equipped with Supelco purge trap K, packed with Carbopack B/Carboxen 1000 & 1001 (VOCARB 3000).

Autosampler- Archon Model 5100 water autosampler. The sampling tray has a 50 vial capacity and is capable of adding 1 µL internal standard and surrogate standard to the sample.

Agilent MSD ChemStation Software for data collection.

Column choices:
DB-624 (Agilent # 121-1324), 20 meter, 0.18 mm ID, 1.0 µm df.
Maximum Temperature: 280ºC.

Rxi-624SilMS (Restek# 13868), 30 meter, 0.25 mm ID, 1.4 µm df.
Maximum temperature: 320ºC.

RTX-502.2 (Restek # 40915), 40 meter, 0.18 mm id, 1.0 µm df.
Maximum Temperature: 270ºC.

Carrier Gas: Helium (high purity 99.999%)

Instrument Operating Parameters

Archon and Tekmar Purge and Trap Conditions:
Carrier gas: Helium (high purity 99.999%)
Flow rate: 40 mL/minute
Sample size: 25 mL
IS & Surrogate amount: 1 µL

Purge: 0º for 11 minutes
Dry Purge: 2 minutes
Desorb: 255º for 3 minutes
Bake: 260º for 10 minutes

DB-624/Rxi-624SilMS Inlet:
Mode: Split.
Initial Temperature: 180ºC.
Pressure: 7.17 psi.
Split Ratio: 15:1
Split Flow: 15.0 mL/minute.
Total Flow: 19.0 mL/minute.
Gas Saver Mode: On.
Saver Flow: 20.0 mL/minute.
Saver Time: 2.00 minutes.
Gas Type: Helium.

RTX-502.2 Inlet:

Mode: Split.
Initial Temperature: 180ºC.
Pressure: 33.83 psi.
Split Ratio: 30:1
Split Flow: 30.0 mL/minute.
Total Flow: 33.5 mL/minute.
Gas Saver Mode: On.
Saver Flow: 20.0 mL/minute.
Saver Time: 2.00 minutes.
Gas Type: Helium.

Columns:
Flow Control Mode: Constant Flow
Initial Flow: 1.0 mL/minute.
Average Velocity: 31-36 cm/second.

Detector/Aux:
Temperature: 230º C for DB-624/Rxi-624SilMS.
170º C for RTX-502.2
DB-624/Rxi-624SilMS Temperature Program:

35º C, hold for 4 minutes
35-220º at rate of 15º C/minute

Equilibration Time: 0.50 minutes.
Post Time: 0.0 minutes.
Total Run Time: 16.33 minutes.

RTX-502.2 Temperature Program:

35º C, hold for 4 minutes
35-150º at rate of 6º C/minute
150-220º at rate of 8º C/minute

Equilibration Time: 0.50 minutes.
Post Time: 0.0 minutes.
Total Run Time: 31.92 minutes.

Mass Spectrometer Conditions:

Acquisition Mode: Scan
Low Mass: 35 AMU
High Mass: 280 AMU
MS Quad Temperature: 150º C
MS Source Temperature: 230º C
Solvent Delay: 0 minutes

7. Reagents, Standards, and Solutions

7.1. Reagents

- Organic-Free Water: Water free of interferences above the analyte reporting limits. Organic-free water that has passed through a bed of activated charcoal is used for this method. Charcoal is changed when contaminants are above the reporting limit for VOC's.

- Methanol: HPLC Grade (Fisher Scientific, Cat. # A452SK-4).

- Hydrochloric Acid (1:1): Add measured volume of concentrated HCl to equal volume of Organic Free water.

- Sodium Thiosulfate ($Na_2S_2O_3$), ACS Reagent Grade, granular.

7.2. Certified Stock Standards

VOC Liquids/Gases Stock Standard Set
54 Liquid and 6 Gas Component Set, (1 ampule each). M-502A-R/B-10X-SET, AccuStandard Inc, 125 Market Street, New Haven, CT 06513. Concentration: 2.0 mg/mL in MeOH.

MtBE Stock Standard
MtBE. S-078-10X, AccuStandard Inc, 125 Market Street, New Haven, CT 06513. Concentration: 2.0 mg/mL in MeOH.

n-Hexane Stock Standard
*n-Hexane***.** TK-100-01S-10X, AccuStandard Inc, 125 Market Street, New Haven, CT 06513. Concentration: 2.0 mg/mL in MeOH.

524.2 Fortification Solution Stock Standard (IS/SS)

Composed of *Fluorobenzene, 4-Bromofluorobenzene, and 1,2-Dichlorobenzene-d_4*. M-524-FS, AccuStandard Inc, 125 Market Street, New Haven, CT 06513. Concentration: 2.0 mg/mL in MeOH.

Quarterly Control Standards
Individual standards are purchased for each target analyte. Concentrations vary by lot number. *Regulated VOC's,* QCO-007-12, *Unregulated VOC's,* QCO-007-3, *Trihalomethanes,* QCO-002. NSI Solutions Incorporated, 7212 ACC Blvd., Raleigh, North Carolina 27617.

7.3. Preparation of Working Standards

All solutions described in this section are stored in a freezer at <0 °C and protected from light. Expiration dates are one month from preparation or the vendor expiration for the certified standard, whichever comes first.

Internal Standard/Surrogate Solution (25 µg/mL, all components)
A working standard is prepared by transferring 625 µL of fortification solution stock standard (2000 mg/mL) to a 50mL volumetric flask containing approximately 40mL MeOH. Fill to volume with MeOH, stopper, and invert three (3) times. Transfer to a properly labeled bottle or bottles. A 1 µL aliquot of this solution added to a 25 mL water sample gives a concentration of 1 µg/L of each component.

524.2 Gases Standard Solution (200µg/mL)
A working standard is prepared by transferring 1 mL of 524.2 Gases stock standard (2000 mg/mL) to a 10mL volumetric flask containing approximately 4 mL MeOH. Fill to volume with MeOH, stopper, and invert three (3) times. Transfer to a properly labeled bottle or bottles.

524.2 Liquids/Hexane Standard Solution (200µg/mL)
A working standard is prepared by transferring 1 mL of 524.2 Liquids stock standard (2000 mg/mL) and 1 mL of n-Hexane stock standard (2000 mg/mL) to a 10mL volumetric flask containing approximately 4 mL MeOH. Fill to volume with MeOH, stopper, and invert three (3) times. Transfer to a properly labeled bottle or bottles.

MtBE Standard Solution (200µg/mL)
A working standard is prepared by transferring 1 mL of MtBE stock standard (2000 mg/mL) to a 10mL volumetric flask containing approximately 4 mL MeOH. Fill to volume with MeOH, stopper, and invert three (3) times. Transfer to a properly labeled bottle or bottles.

7.4. Standard Labeling, Record Keeping and Replacement

Labeling
Each individual standard solution (calibration and all control solutions) is labeled with the unique laboratory identifier, contents of the solution, lab expiration date, and the initials of the analyst who prepared the solution.

Record Keeping
A notebook is kept for recording the date of preparation of standard calibration solutions, method of preparation, identifying number, and expiration date. This notebook is kept in the Volatile Organics Laboratory.

Replacement
Stock standard solutions are to be replaced sooner than the one-month expiration date if comparison with laboratory fortified blanks, or QC samples indicate a problem.

Expired Stock Standards
Expired stock standards are **NOT** used for preparation of calibration solutions or for any other control solution. Expired stock standards and solutions are discarded into appropriate hazardous waste containers. When filled, containers are stored in the Hazardous Waste Storage area and manifested according to Laboratory policy.

8. Sample Collection, Preservation and Handling

The laboratory staff prepares bottle orders for all sampling events. Three (3) 40mL amber borosilicate screw cap vials with Teflon-silicone septa lined caps are used for each field sample. In addition, field blank bottles must be prepared for each sampling event. Field blanks are prepared by filling two (2) sampling bottles with Organic-free water.

All volatile samples, except Trihalomethanes, are preserved with 1:1 HCl (4 drops/40mL). The sample pH must be <2.

Method parameters call for the addition of sodium thiosulfate to sample vials prior to sampling for chlorinated water systems. Sodium thiosulfate is a dechlorinating agent added to prevent reactions that may occur between residual chlorine and indeterminant contaminants present in some solvents, yielding compounds that may subsequently interfere with the analysis. If sampling for TO2 (Trihalomethanes), use this preservation method.

At this time, the vast majority of laboratory samples come from un-chlorinated sources. As such, the addition of sodium thiosulfate is not necessary for samples from these locations. When preparing vials for sampling events

at facilities where chlorine is known or suspected to be present, 3 mg of sodium thiosulfate (Section 7.1) is added to each empty vial prior to sample collection. After collection, the sampler needs to acidify the sample with 4-5 drops of 1:1 HCl. Any time chlorinated samples are received in the laboratory, all calibration and quality control samples associated with those samples must also be prepared with sodium thiosulfate.

Sample vials should be filled to the top without any air bubbles. After collection, samples should be chilled to 4ºC. Upon receipt in the laboratory, samples are stored at 4º C in a laboratory refrigerator. All samples must be analyzed within 14 days of collection. If a sample is received without any preservative, it must be analyzed within 24 hours.

Sample bottle labels contain the following information:

RI Department of Health Laboratory ( ) Legal TO
Sample #_____Date/Time Collection_____
Collection Point:_____
Collector:_____Program:_____
Preservation Added: HCl
(X) by laboratory ( ) by collector

9. Calibration and Standardization

In this method, the analytical system is calibrated via internal standards. In this technique, five calibration standards are prepared for each analyte of interest by adding volumes of the calibration standard solutions to acidified organic-free water in volumetric flasks. The lowest standard represents analyte concentrations at the reporting limit. The remaining standards bracket the analyte concentrations expected in the sample extracts. Each aqueous calibration standard is then processed through the entire analytical procedure.

9.1. Preparation of Calibration Standards

Take three (3) 200mL volumetric flasks, add 10 drops of 1:1 HCl and fill completely with organic-free water. Also, take two (2) 100 mL volumetric flasks, add 5 drops of 1:1 HCl and fill completely with organic-free water. Each flask represents a level on the calibration curve. Spike each vial with the appropriate amount of calibration standard as follows:

Calibration Curve Level	Spiking Volume of each standard: Liquids, Gases, and MtBE (µL)	Final Volume (mL)	Concentration of Calibration Curve Std. (µg/L)
1	0.5	200	0.5
2	2.0	200	2.0
3	5.0	200	5.0
4	4.0	100	8
5	5.0	100	10

Be sure to inject the standard into the water and to cap the flask between additions of standards. Stopper and mix each volumetric flask by inverting three times. Prepare and label two (2) 40 mL VOA vials per standard. Pour standards into appropriate vials. Make sure none of the standards have any bubbles in the vials before proceeding, if they do, pour more standard into the vial until no bubbles are present.

9.2. Calibration Standard Analysis

After the analysis of the BFB tune and LRB, analyze each calibration standard, according to Section 11, starting with the standard of lowest concentration. LRB's should be analyzed after Cal level 4 and Cal level 5 to ensure there is no carryover between the two (2) higher level standards. Using the Agilent MSD Chemstation data analysis software, use Average Response Factor for the calibration curve for each target analyte. The %Relative Standard Deviation (%RSD) for each analyte and surrogate must be ≤20%.

Calibration curves are run before each set of samples, however an existing calibration curve may be used if it is verified before any samples are analyzed. Existing curves are verified by analyzing continuing calibration verification standards (CCV) at the beginning and end of the analysis. In order to be deemed passing, analyte responses in the CCV must not vary from the true value by more than ±30%. If the CCV does not pass, a new calibration curve must be prepared and analyzed.

10.Quality Control

The laboratory performs initial demonstration of capability (IDC) and method detection limit (MDL) studies, as required by the EPA. Data quality is evaluated and documented by continued analysis of a number of different quality control (QC) measures (see below). The laboratory maintains records to document the quality of data that is generated. Data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristic of the method.

Minimum quality control requirements for this method include:

4-Bromofluorobenzene Tune (BFB)
Continuing Calibration Verification Standards (CCVs)
Initial Demonstration of Capability (IDC)
MDL Determination (MDL)
Laboratory Reagent Blanks (LRB)
Field Blanks (FB)
Laboratory Fortified Blanks (LFB)
Laboratory Duplicate (DUP)
Internal and Surrogate Standard (IS/SS)
External Quality Control Sample (QCS)
pH verification (pH)

10.1. 4-Bromofluorobenzene Tune (BFB)

At the beginning of each day that analyses are to be run, a BFB tune must be performed to check GC performance and MS sensitivity. A water blank is analyzed to verify the BFB tune. Use Autofind BFB from the tuner menu and print a report. The Autofind procedure averages three (3) scans at the apex of the peak to produce the BFB spectrum. Manual selection of the apex scans is also allowed. The BFB tune is good for a 12-hour time period, after the 12 hours, a new tune must be performed. BFB must meet the criteria in Table 1. If not, remedial actions must be taken. See Section 10.2.

10.2. Continuing Calibration Verification Standards (CCVs)

CCVs are calibration standards analyzed to substantiate the continued accuracy of the analytical system. If the response for any analyte varies from the true value by more than ±30%, the CCV must be repeated using a fresh calibration standard. If this fails, then a new calibration curve must be generated and the sample set must be re-analyzed with this curve (Section 9).

CCV standards, at the middle calibration concentration level, are run at the beginning of each sample analysis and at the end of the sample analysis. As previously mentioned in Section 9.2, once an acceptable calibration curve has been established, CCVs may be used to verify the working calibration curve instead of creating a new curve to run with the samples.

Because of the large number of target analytes and QC in this method, some latitude is given when evaluating the CCV or LFB data. All regulated analytes MUST be within the ±30% criteria. If 10% or more of the unregulated analytes are not within the specified criteria or if the criteria for any analyte are grossly exceeded (≥40%), corrective action must be taken. If an unregulated analyte QC is only slightly beyond the

±30% criteria, this will be noted and deemed acceptable. Also, repeated failure of a particular analyte or analytes must result in corrective action, for example; new standards and/or new curve.

Possible remedial actions for (1) BFB tune does not meet criteria in Table 1, (2) the CCV fails, (3) the sensitivity cannot be adjusted with EM voltage to achieve satisfactory sensitivity, and/or (4) surrogate recovery or LFB's indicate the system is out of control, are listed below:

- Check and adjust GC and/or MS operating conditions.
- Prepare fresh standards and repeat initial calibration.
- Clip a short portion of the column from the injector end, or change column.
- Clean the MS source.
- Replace the trap for the Purge & Trap system.
- Check other components of the MS, such as the electron multiplier.

If analyzing for THMs (TO2), the beginning CCV for each analysis batch must be at or below the minimum reporting level to verify instrument sensitivity. The low level CCV (LLCCV) would be 1 µg/L, see table below in how to make this standard. Recoveries for this standard must be within ±50%. Subsequent CCVs should be at the 5 µg/L level and have recoveries of ±30% of their true values.

Preparation and Analysis

Prepare one (1) 200 mL aliquot of organic-free water acidified with 10 drops of 1:1 HCl, at a low-level concentration by spiking the water with the appropriate amount of calibration standard solution listed below.

Analyte	Spiking Volume of Calibration Std. (µL)	Concentration of LLCCV (µg/L)
Liquids	1.0	1.0

10.3. Initial Demonstration of Capability (IDC)

Initial demonstrations of capability are performed to verify and document that laboratory procedures are capable of meeting performance criteria as outlined in the method. Individual analysts must demonstrate proficiency with the analytical techniques prior to generating data for environmental samples.

Preparation and Analysis

Prepare one (1) 200 mL aliquot of organic-free water acidified with 10 drops of 1:1 HCl, at a mid-level concentration by spiking the water with the appropriate amount of calibration standard solution listed below.

Analyte	Spiking Volume of Calibration Std. (µL)	Concentration of IDC (µg/L)
Liquids	5.0	5.0
Gases	5.0	5.0
MtBE	5.0	5.0

Stopper and invert the volumetric flask three times and put into four (4) VOA vials. Analyze the IDCs according to the procedure in Section 11.

Data Evaluation
For each analyte, the mean percent recovery for all four samples must fall in the range of ± 20%, and the %RSD of all four values must be 20% or less. For those compounds that meet the acceptance criteria, performance is judged acceptable and sample analysis may begin. For those compounds that fail these criteria, this procedure must be repeated using four fresh samples until satisfactory performance has been demonstrated.

IDC standards must be repeated each time the significant GC hardware or analytical conditions are modified.

10.4. MDL Determination (MDL)

Principle of the MDL Calculation: The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero and determined from analysis of a sample in a given matrix containing analyte.

Preparation and Analysis
Prepare two (2) 200 mL aliquots of organic-free water at a concentration twice the lowest calibration standard by spiking the reagent water with the appropriate amount of calibration standard solution listed below.

Analyte	Spiking Volume of Calibration Std. (µL)	Concentration of MDL (µg/L)
Liquids	1.0	1.0
Gases	1.0	1.0
MtBE	1.0	1.0

Stopper and invert the volumetric flask three times and put into four (4) VOA vials. Analyze the MDL samples along with a laboratory reagent blank according to the procedure in Section 11. MDL determination must be repeated annually for each instrument.

Data Evaluation
Using the calibration curve, calculate the average concentration in µg/L and the standard deviation of the concentrations for each analyte. For each analyte, the MDL must be less than the reporting limit. Use the standard deviation to calculate the MDL:

MDL = 3.143 * standard deviation
(Where 3.143 = t value for 99% confidence level and 7 trials)

10.5. Laboratory Reagent Blanks (LRB)

The LRB is an aliquot of organic-free water that is treated exactly as a sample. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or other apparatus. If a LRB produces a peak within the retention time window of any analyte that might prevent the determination of that analyte, the source of contamination is identified and eliminated before processing samples. One LRB must be run with each 12-hour batch or with every 20 samples analyzed.

Preparation and Analysis
LRBs are prepared by filling empty sample vials with organic-free water or by using the Archon to bring the water to the purge &trap. Analyze according to the procedure outlined in Section 11.

Data Evaluation
The concentration of any analyte detected in the LRB should not exceed the RL of that analyte. If the concentration of any analyte in the LRB exceeds the RL, samples containing that analyte must be reanalyzed after the source of the contamination has been found. If the concentration of any analyte in the LRB exceeds the RL, but is not present in any samples, then the samples do not have to be reanalyzed. In this instance, a corrective action report will be written and included with the sample report.

10.6. Field Blanks (FB)

The FB is an aliquot of reagent water prepared in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation and all analytical procedures. The FB serves the same function as an LRB, to determine if method analytes or other interferences are present laboratory environment, reagents, or other apparatus. In addition, the FB is used to determine if method analytes or interferences are present in the field environment. If a FB produces a peak within the retention time window of any analyte that might prevent the determination of that analyte, the source of contamination is identified and eliminated before processing samples.

Preparation and Analysis
As described in Section 8, FBs are prepared by filling an acidified sample vials with organic-free water. One set (2 vials) of FBs are included with each sampling event. FBs are analyzed along with their associated field samples according to the procedure outlined in Section 11.

Data Evaluation
The concentration of any analyte detected in the FB should not exceed the RL of that analyte. If the concentration of any analyte in the FB exceeds the RL, samples containing that analyte must be reanalyzed after the source of the contamination has been found. If the concentration of any analyte in the FB exceeds the RL, but is not present in any samples, then the samples do not have to be reanalyzed. In this instance, a corrective action report will be written and included with the sample report.

10.7. Laboratory Fortified Blank (LFB)

LFB samples are aliquots of reagent water spiked with target analytes and carried through every aspect of the procedure. LFB samples are analyzed to monitor the accuracy of the analytical procedure, independent of matrix effects.

LFB samples are fortified to contain target analytes at a concentration of the mid-level calibration standard and must be analyzed at a frequency of 5% of samples analyzed, or at least one (1) per batch, whichever is greater.

Preparation and Analysis
The LFB is prepared by spiking 200mL of acidified organic-free water with the appropriate amount of calibration standard solution listed below.

Analyte	Spiking Volume of Calibration Std. (µL)	Concentration of LFB (µg/L)
Liquids	5.0	5.0
Gases	5.0	5.0
MtBE	5.0	5.0

Stopper and invert the volumetric flask three times and put into four (4) VOA vials. Analyze the LFB sample along with field samples according to the procedure in Section 11.

Data Evaluation
The recoveries for the LFB should be ± 30 %. If any analytes are outside this range, stop the analysis and repeat the LFB. See Section 10.2 for exceptions to the acceptance of the LFB.

10.8. Field Sample Duplicate (DUP)

Field sample duplicates are two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of the duplicate samples give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

Preparation and Analysis
Field duplicates are analyzed according to the procedure outlined in Section 11.

Data Evaluation
Calculate the relative percent difference between the original sample and the field duplicate. Acceptance criteria for duplicates with concentrations of 0.5 to 2.0 ppb is ±50% difference. If concentrations are greater than 2.0 ppb, then ±30% difference is used. Significant differences call for reevaluation of sample collection, preservation, and storage practices.

10.9. Internal and Surrogate Standard (IS/SS)

The internal standard (Fluorobenzene) and surrogates (4-Bromofluorobenze and 1,2-Dichlorobenzene-d_4) standard are used to monitor method performance with each sample by determining approximately how much recovery (or loss) may have occurred during analysis. The internal and surrogate solution is added to each sample and taken through the entire sample analysis procedure. The expected concentration in each sample is 1.00µg/L.

Preparation and Analysis
1µL of the IS/SS is automatically added to the 25mL aliquots of all QC samples (BFB, LRB, CCV, LFB, DUP, QCS) and field samples by the Archon autosampler.

Data Evaluation
The internal standard area response must not have deviated by more than 30% from the area measured in the last CCV, or by more than 50% from the area measured during initial calibration. Acceptable recovery for the surrogate standard is ± 30% of 1.00 µg/L. Samples that fall outside this range must be reported as suspect due to unacceptable recovery.

10.10. Quarterly Quality Control Sample (QCS)

The QCS is used to check the concentration of the calibration and quality control standards by comparing them to externally prepared test materials. QCS' are prepared and analyzed at least quarterly. The QCS is

prepared from reference material obtained from an independent source different from the source from which the stock solutions are purchased (NSI Solutions, Inc, Raleigh, NC or Environmental Resource Associates, Arvada, CO, or other reputable vendor).

Prepare the quarterly QCS sample according to instructions provided by the manufacturer. Analyze the sample in the same manner as field samples. Results must be within the quality control limits established by the manufacturer.

10.11. pH Verification (pH)

All acidified sample vials that are analyzed must be checked for pH and recorded in the pH logbook, located in room 415. The pH should be <2. If the pH is not <2, analyze the second vial of that sample. If the pH for the second vial is not <2, inform the Drinking Water Quality (DWQ) office or the submitting agency. The results will be reported as "SPU" (sample preservation unacceptable) or "questionable" for this sample.

10.12. Control Charts

Control charts are used to demonstrate that the analytical process is in statistical control, and to detect any tends or bias. If trends are detected, they are corrected before an "out of control" situation occurs. Control charts may be generated within the current LIMS being used at the laboratory.

10.13. Frequency and Limits of Acceptability

QC Standard	Description	Frequency	Acceptance Criteria	Corrective Action
Linear Calibration Curve	Calibration of Analytical System	Prior to sample analysis. Once established, a CCV may be analyzed to verify the existing curve	All analytes and surrogates must have %RSD <20%	Repeat. Prepare new standard. Prepare a new calibration curve. Perform instrument maintenance.
Continuing Calibration Standard (CCV)	Level 3 of calibration curve, 5ppb	Run before and after samples and QC (within 12 hour tune time).	<30% deviation from ICAL response factors, IS and surrogate areas	Repeat. Prepare new standard. Prepare a new calibration curve. Perform instrument maintenance.
BFB tune	Mass Spectrometer check	At the beginning of every analysis batch. Must be repeated after 12 hours.	Must pass key ion criteria	Repeat. Prepare new standard. Perform instrument maintenance.
Initial Demonstration of Capability	Four aliquots of laboratory fortified blank	Upon implementation of method or after significant changes to method	= ±20% mean of true value and ≤20% RSD	Repeat with four samples until performance is satisfactory.
MDL	Seven aliquots of fortified reagent blank	Annually or if there are major changes to method or equipment	Must be less than the reporting limit of the analyte	Repeat the analysis using seven samples.
Laboratory Reagent Blank (LRB)	Reagent water that is treated exactly as a sample to determine if there are interfering peaks	One with each set of samples analyzed or 5% of samples, whichever is greater.	Analytes must not be present above reporting limit of 0.5ppb	LRB and its associated samples must be reanalyzed.
Laboratory Fortified Blank (LFB)	Assesses method and laboratory performance	One with each set of samples analyzed or 5% of samples, whichever is greater.	70-130% Recovery	LFB and its associated samples must be reanalyzed.
Field Sample Duplicate (DUP)	Assesses matrix effects on analyte recovery.	5% 0f the routine samples or one per sample set, whichever is greater.	±50% for samples with concentrations of 0.5-2ppb. If >2ppb, then ±30%.	Significant differences call for reevaluation of sample collection, preservation, and storage practices.
Field Reagent Blank	Reagent water that is sent to the field during sample collection, treated exactly the same as a sample.	One with each set of field samples collected	Analytes must not be present above reporting limit of 0.5ppb	Evidence of contamination requires resampling
Surrogates	Monitors method performance	Added to all field samples and QC samples	70-130% recovery	Reanalysis or resampling is necessary
Quality Control Sample	External QC sample used to check lab performance with externally prepared test materials	At least quarterly	Within ranges specified by the manufacturer	Reanalyze QCS or purchase new QCS from vendor. Prepare new calibration curve.

Low Level Check for THM analysis	Verifies quantitation of THMs at the reporting level	One with each batch of samples when THM analysis is requested	+/-50% of expected value	Repeat. Prepare new standard. Prepare a new calibration curve. Perform instrument maintenance.
Internal Standards	Monitors method performance	Added to all field and QC samples	Area counts differing no more than +/-30% from last CCV or +/-50% from last ICAL	Repeat. Prepare new standard. Prepare a new calibration curve. Perform instrument maintenance.

11. Analytical Procedure

Prior to starting the analytical procedure, make sure that the Archon water reservoir bottle is at least half full with organic-free water and the waste bottle is empty. BFB tune is only good for a 12 hour analytical batch; keep this in mind when selecting samples and making the sequence.

11.1. Instrument Initialization & Sequence Setup

As you prepare the GC/MS for analysis, bake out the trap in the purge & trap. In the Tekmar software, click on 'Commands', 'Goto Bake'. Make sure that the bake temperature is no higher than 260º. After bake out is complete, make sure purge & trap method is set at VOA desorb3.mvsa for the Stratum and 524 3MINDES.mvsa for the Velocity.

If not already running, open the MSD ChemStation instrument software. Once all connections have been established, enter the software and go to: Method / Load Method. The current GC method used to analyze samples is 624SIL1.M (column: Rxi-624SilMS), 524DB624.M (column: DB-624), and 524LOW.M (column: RTX-502.2). Loading the method automatically directs the GC to establish the proper inlet, gas flow and oven conditions for sample analysis.

Next, create a sample sequence. Creating sequences in the ChemStation software allows for the automated analysis of samples. Sequences tell the GC system to automatically inject each sample, and to acquire and analyze the data according to the specified method. There are two principal menus used to create sequences, "Sample Log Table" and "Run Sequence".

It is often easier to create a new sequence for a new batch of samples by editing a previous sequence. To load a previous sequence, enter the software and go to: Sequence / Load Sequence. Then load the most recent sequence. Sequences are named by date, so the first sequence analyzed on August 1st 2011, would be named 080111A.

- Enter the "Sequence Log Table" field (Sequence / Edit Sequence). The sequence table lists each sample in the sequence in the order it will be run and contains the necessary sample type designation, vial number, method, and data file information for each sample.

- All sequences should begin with a BFB tune.

- Fill out the table to run the calibration standards, QC and field samples. Each sequence should have a BFB, initial and final CCV, LRB, and LFB included in the run. LFB should be analyzed midway through the run. Before any samples can be analyzed, a BFB tune, CCV, and LRB must be run, analyzed, and deemed acceptable. Each "Sample" at minimum needs a sample type designation, vial number, name, method, and unique data file identifier. Data file names are assigned in the same manner as sequences.

- Open the "Run Sequence" menu (Sequence / Run Sequence). Specify where the sample data files will be stored by entering the name of a folder in the "Data File Directory" field. Generally data files are stored by analysis date in folders named for the date in the same manner as sequences (i.e. 060509). Entering a new folder name will automatically trigger the software to create a new folder. Click "OK".

- Save the new sequence (Sequence / Save Sequence) according to the date and close the window. Next, load the sequence (Sequence / Load / Select from Menu) to be sure the software is referencing the updated sequence. Print two copies of the sequence (Sequence / Print Sequence). One copy goes with the data packet and the other goes in the instrument run log notebook.

11.2. Sample Preparation

- There is no special sample preparation for the VOA analysis that does not require a dilution. However, you will want to make sure that the label is uniformly placed on the vial. The Archon may jam if the label has edges sticking up or if the label is not smooth.

- If a dilution is needed for the sample, the Archon is capable of performing dilutions of 2, 5, 10, 20, 50, and 100X. If a greater dilution is needed, the analyst will have to make the dilution in a volumetric flask and then transfer the solution to a 40 mL VOA vial for analysis.

11.3. Autosampler Set-Up

- Currently, we are using Method 20 on the Archon for the BFB tune. This method is set up to take water from the water bottle and run it as a blank, so no sample vial is needed. On the autosampler keyboard follow this sequence to set up the method, if needed. After each step, press ENTER.
    - Press METHOD, 20.
    - Edit method.

- Sample type: BLANK
- First vial: 01. Last vial: 01
- Sample volume: 25
- Rinse volume: 25
- # rinses: 01
- Standard 1: No. Standard 2: Yes. (One of these, not both, needs to be yes, whichever reservoir has the IS/SS in it).
- Syringe flushes: 00
- Desorb time (m): 03.0 (this number needs to be the same as the desorb time in the purge and trap method being used).
- Oper. Mode: remote
- Cycle timer: 00.0
- Aux. Timer: 00.0
- Link to method: 00 (or 01, if running samples right after the BFB tune)
- Press METHOD: edit blank vials.
- Blank: Yes or No, depending if you want two (2) blanks run or just one.
- Press METHOD 2x, this brings you back to the home page of the LCD display.

- Method 01 is set-up to run samples with no dilutions. The method is as follows, press ENTER after each entry:
  - Press METHOD, 01.
  - Edit method.
  - Sample type: WATER
  - First vial: 01. Last vial: 10 or however many samples you will be running.
  - Sample volume: 25
  - Dilution factor: NO, for no dilution.
  - Rinse volume: 25
  - # rinses: 01
  - Standard 1: No. Standard 2: Yes. (One of these, not both, needs to be yes, whichever reservoir has the IS/SS in it).
  - Stir: No
  - W. stir time (m): 0.0
  - Syringe flushes: 00
  - Desorb time (m): 03.0 (this number needs to be the same as the desorb time in the purge and trap method being used).
  - Oper. Mode: remote
  - Cycle timer: 00.0
  - Aux. Timer: 00.0
  - Link to method: 00 (or 02, if you need to link to a method with a dilution).

- Press METHOD: edit blank vials.
- Blank: Yes or No, depending if you want to run a blank after any of the samples. Change to yes, if you want to run an LRB after a sample, (e.g.: vial 08, YES. Vial 09, NO).
- Press METHOD 2x, this brings you back to the home page of the LCD display.

- The Archon autosampler will automatically withdraw 25 mL of sample and deliver it to the Tekmar purge and trap sparge cell, along with 1 µL of internal standard and surrogate from the standard reservoir. 25 ng of each compound is added into the water.

- Load samples into the autosampler tray as you have ordered them in the sequence.

11.4. Starting the Run

- Make a check to ensure that the GC method is correct, that the sequence table includes all necessary samples and information, and that all VOA vials are in the correct positions.

- Make sure the Archon autosampler reservoirs have enough IS/SS solution in them for the sample run.

- Enter the GC software and start the sequence (Sequence / Run Sequence). The sequence will not start on the GC until the sample is desorbed from the purge and trap.

- On Archon, press AUTO, method number: 20, ENTER. Start auto-run: ENTER.

12. Identification Of Analytes and Calculations

Sample components are identified by comparing their mass spectrum (after background subtraction) to a reference spectrum in the user created database plus by comparing their retention times to the retention times of target compounds in reference standard chromatograms. In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample.

Identification, integration and quantitation of peaks are done using Agilent ChemStation Data Analysis software. The concentration of each analyte is derived directly from the internal standard calibration curve.

Identification requires expert judgement when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one component, appropriate analyte spectra and background spectra can be selected to identify the analyte.

If a target analyte is detected in the sample with a concentration that is greater than the highest standard in the calibration, the sample must be diluted to a concentration that should fall within the span of the curve. This is done easily by placing another VOA vial (of the same sample) in the Archon autosampler, and then reanalyzing at a dilution.

12.1. Evaluation of BFB Tune

In the ChemStation software, load the datafile for the BFB tune. In the tuner menu, use Autofind BFB to screen, and look at the report. The Autofind procedure averages three (3) scans at the apex of the peak to produce BFB spectrum. Manual selection of the apex scans is also allowed. BFB must pass the criteria in Table 1.

If any criteria are not met, the MS must be retuned. Refer to BFB target or Autotune in software to re-tune, or to adjust parameters.

Once new tune parameters are chosen, save tune file as BFB080111.U (refers to august 01, 2011). Make sure to link the tune file name with the method you are using for analysis. Select instrument, MS tunefile, and then click on the saved tune file, and save the method.

Re-run a water blank to verify the tune is acceptable.

13. Preventive Maintenance

There are several routine maintenance procedures for the GC/MS system, including inlet maintenance, source cleaning, column clipping or replacement, and trap replacement. Specific instructions are listed in the Agilent or Tekmar Manual. All information is written in the maintenance logbook for each instrument, including analyst's name, description of work performed, and date of the work.

Preventive maintenance is performed yearly as part of the service contract kept on the Agilent GC/MS system. This service is performed by Agilent engineers. Their work is recorded and logged into the maintenance logbook kept in the Laboratory.

Table 1. Ion Abundance Criteria for BFB

Mass	M/Z Abundance Criteria
50	15 to 40 percent of mass 95

75	30 to 80 percent of mass 95
95	Base Peak, 100 percent relative abundance
96	5 to 9 percent of mass 95
173	Less than 2 percent of mass 174
174	Greater than 50 percent of mass 95
175	5 to 9 percent of mass 174
176	Greater than 95 but less than 101 percent of mass 174
177	5 to 9 percent of mass 176

Appendix A:

Group	Name	No.
TO 2	Chloroform	1
Trihalomethanes	Bromodichloromethane	2
	Dibromochloromethane	3
	Bromoform	4
	Total Trihalomethanes	5
TO3		
Private Wells	Chloromethane	1
	Vinyl Chloride	2
	Bromomethane	3
	Chloroethane	4
	1,1-Dichloroethene	5
	Methylene Chloride	6
	1,2-Dichloroethene	7
	Methyl tert Butyl Ether	8
	Hexane	9
	1,1-Dichloroethane	10
	Chloroform	11
	1,1,1-Trichloroethane	12
	Carbon Tetrachloride	13
	Benzene	14
	1,2-Dichloroethane	15
	Trichloroethene	16

	1,2-Dichloropropane	17
	Bromodichloromethane	18
	Cis-1,3-Dichloropropene	19
	Toluene	20
	Trans-1,3-Dichloropropene	21
	1,1,2-Trichloroethane	22
	Tetrachloroethene	23
	Dibromochloromethane	24
	Chlorobenzene	25
	Ethylbenzene	26
	m+p –Xylene	27
	o-Xylene	28
	Bromoform	29
	1,1,2,2-Tetrachloroethane	30
	1,3-Dichloropropene(total)	31
	Xylenes, total	32
TO4		
Private Wells	TO3 List + Petroleum Hydrocarbons	33

Group	Name	No
TO12	**benzene**	1
	bromobenzene	2
	bromochloromethane	3
	bromodichloromethane	4
	Bromoform	5
	Bromomethane	5
	n-butylbenzene	7
	sec-butylbenzene	8
	tert-butylbenzene	9
	carbon tetrachloride	10
	Chlorobenzene	11
	Chloroethane	12
	Chloroform	13
	Chloromethane	14
	2-chlorotoluene	15
	4-chlorotoluene	16
	dibromochloromethane	17
	dibromomethane	18
	1,2-dichlorobenzene	19
	1,3-dichlorobenzene	20
	1,4-dichlorbenzene	21

	Dichlorodifluoromethane	22
	1,1-dichloroethane	23
	1,2-dichloroethane	24
	1,1-dichloroethene	25
	cis-1,2-dichloroethene	26
	trans-1,2-dichloroethene	27
	1,2-dichloropropane	28
	1,3-dichloropropane	29
	2,2-dichloropropane	30
	1,1-dichloropropene	31
	cis-1,3- dichloropropene	32
	trans-1,3-dichloropropene	33
	Ethylbenzene	34
	Hexachlorobutadiene	35
Group	**Name**	**No**
TO12 continued	Hexane	36
	Isopropylbenzene	37
	4-isopropyltoluene	38
	Methyl tertiary butyl ether	39
	methylene chloride	40
	naphthalene	41
	n-propylbenzene	42
	Styrene	43
	1,1,1,2-tetrachloroethane	44
	1,1,2,2-tetrachloroethane	45
	Toluene	47
	1,2,3,-trichlorobenzene	48
	1,2,4-trichlorobenzene	49
	1,1,1-trichloroethane	50
	1,1,2-trichloroethane	51
	trichloroethene	52
	trichlorofluoromethane	53
	1,2,3-trichloropropane	54
	1,2,4-trimethylbenzene	55
	1,3,5-trimethylbenzene	56
	vinyl chloride	57
	o-xylene	58
	m+p-xylene	59
	Xylenes (total)	60
	1,2-Dibromoethane	61
	1,2-dibromo-3-chloropropane	62
	1.3-dichloropropene	63

TO 17	TO12 List + Petroleum Hydrocarbons	64