Purgeable organic compounds, total recoverable, gas chromatographic/ mass spectrometric, purge and trap (0-3115-83)

Parameter Code

Chloromethane---------- 34418
Bromomethane---------- 34413
Vinyl chloride ----------39175
Chloroethane ----------34311
Methylene chloride ----------34423
1,1-Dichloroethene ----------34501
1,1-Dichloroethane ----------34496
Trans-1,2-Dichloroethene----------34546
Chloroform----------32106
1,2-Dichloroethane ----------32103
1,1,1-Trichloroethane ----------34506
Carbon tetrachloride----------32102
Bromodichloromethane----------32101
1,2-Dichloropropane ----------34541
Trans- 1,3-Dichloropropene ---------- 34699
Trichloroethene---------- 39180
Dibromochloromethane----------32105
Benzene ----------34030
1,1,2-Trichloroethane ----------34511
Cis-1,3-Dichloropropene ----------34704
2-Chloroethylvinyl ether ----------34576
Bromoform ----------32104
1,1,2,2-Tetrachloroethane---------- 34516
Tetrachloroethene---------- 34475
Toluene ---------- 34010
Chlorobenzene ----------34301
Ethylbenzene ----------34371

1. Application

This method is suitable for the determination of purgeable organic compounds in water and watersuspended-sediment mixtures containing at least 3 µg/L of a reportable analyte.

2. Summary

A water sample is purged with helium. The purgeable organic compounds are carried with helium and trapped on a porous polymer trap. The trapped compounds are thermally desorbed into the gas chromatograph. These compounds are separated by gas chromatography (GC) and detected by mass spectrometry (MS).

3. Interferences

3.1 Any purgeable compound that elutes at a retention time similar to that of the analyte and produces an ion that is the same as the quantitation ion of the analyte is a potential interference. Common laboratory solvents such as methylene chloride, benzene, and chloroform may contaminate the sample and give erroneous results.
3.2 Special handling of samples, such as storage in a dessicator over activated charcoal, may be required to prevent contamination by common laboratory solvents.

4. Apparatus

4.1 Gas chromatograph/mass spectrometer/ data system, Finnigan 3223, or equivalent.
4.1.1 Gas chromatographic column, borosilicate glass, 1.8 m x 2 mm id (inside diameter) that has been deactivated and packed with 1 percent SP- 1000 coated on 60/80 mesh Carbopack B, or equivalent.
4.1.2 Gas chromatographic conditions : GC conditions need to be optimized for each system. Use the purgeable standards (see step 5.3) to adjust con ditions to obtain good peak separation in a reasonable amount of time. The following conditions should serve as a starting point for the optimization process:

Injector temperature----- 200°C
Carrier gas flow (He) ---- 20 mL/min
Initial hold temperature -- 45°C
Initial hold time -------- 4 min
Program rate ---------- 8°C/min
Final temperature- - - - - - - 21WC
Final hold time --------- To end of data acquisition

4.1.3 Mass spectrometer conditions: Analyze the mass range 35-260 amu (atomic mass units) with a nominal electron energy setting of 70 eV at a scan rate sufficient to obtain a minimum of 5 scans per chromatographic peak.
4.2 Purge and trap device, Chemical Data Systems model 310, or equivalent: The trap is packed with the following adsorbents: 1 cm methyl silicone coated packing (3 percent SP-2100 on 80-mesh Supelcoport, or equivalent), followed by 15 cm Tenax, and ending with 8 cm silica gel (Davison grade 15), or equivalent. The silica gel may be replaced by 5 cm of Ambersorb resin (Rohm and Haas). New traps are conditioned by heating overnight at 240°C with helium flow (20 mL/min).
4.3 Syringe, gas-tight, 10 mL, equipped with a Teflon syringe valve and a 3-in x 19-gauge needle.

5. Reagents

5.1 BFB (4-Bromofluorobenzene) solution: Fill a 50-mL volumetric flask to the mark with methanol and add a 1.0-µL capillary pipet filled with BFB to the volumetric flask. This solution contains 32 ng BFB per µL.
5.2 Methanol, pesticide analysis quality, Burdick and Jackson, or equivalent.
5.3 Purgeable mixed standards, EPA analytical reference grade or highest purity available: Purgeable standards may be purchased from various commercial sources or prepared from pure compounds. To prepare purgeable mixed standards, fill a 50-mL volumetric flask to the mark with methanol and, for each desired component, add a 1.0-µL capillary pipet filled with the authentic material to the volumetric flask. Mix thoroughly and store at 4°C. Calculate the concentration of each analyte from its density.
5.4 Surrogates/internal standard solution,

bromochloromethane (EPA, or equivalent), 1-bromo-2-chloroethane (EPA, or equivalent), perdeuter obenzene (Pfaltz and Bauer, or equivalent), and fluorobenzene (the internal standard, Aldrich Chemical Co., or equivalent). Add a 1.0-µL capillary pipet filled with each component to a 50-mL volumetric flask filled to the mark with methanol. Mix thoroughly and store at 4°C. Add 5 µL to each sample, standard, and blank to monitor recovery and to provide an internal standard.

5.5 *Water,* organic-free.

6. Procedure

6.1 Condition the trap at 220°C for 10 min.

6.2 Mass spectrometer tuning:

6.2.1 Use perfluorotributylamine to tune the mass spectrometer in a manner that results in a satisfactory calibration of mass assignments as well as agreement with the criteria listed in step 6.2.2.

6.2.2 Set the MS to scan the mass range 35 to 260 amu. Set the GC column temperature to 220-230°C isothermal. Introduce 50 ng of BFB (1.6 µL of solution, step 5.1) by direct, on-column injection
or by purging from 5 mL of reagent water.
Obtain a background corrected mass spectrum of BFB and verify that all of the following criteria are met:

Mass	*Ion abundance criteria*
50	15 to 40 percent of mass 95
75	30 to 60 percent of mass 95
95	Base peak, 100 percent relative abundance
96	5 to 9 percent of mass 95
173	< 2 percent of mass 174
174	> 50 percent of mass 95
175	5 to 9 percent of mass 174
176	> 95 percent but < 101 percent of mass 174
177	5 to 9 percent of mass 176

6.3 Blank analysis:

6.3.1 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the water into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 µL of the surrogate/internal standard solution through the valve, close the syringe valve, and mix.

6.3.2 Transfer 5.0 mL water into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of water for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.3.3 Purge for 11 min.

6.3.4 Immediately begin the desorb cycle and data acquisition when purging is complete.

6.3.5 Begin the temperature program of the GC oven immediately upon completion of the desorb cycle.

6.3.6 Initiate the trap bakeout when data acquisition has ended.

6.3.7 Allow the trap to cool to room temperature and return the GC oven temperature to 45°C for the next analysis.

6.3.8 Analyze the mass spectral data for the three surrogates and the internal standard. Record the integrated area of the quantitation ion for each.

6.3.9 Examine the mass spectral data to verify that the analytical system is free from contamination.

6.4 Calibration:

6.4.1 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the organic-free water into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 µL of surrogate/internal standard solution. Also add 10 µL of purgeable standard solution. Close the syringe valve, and mix.

6.4.2 Transfer 5.0 mL water into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of sample for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.4.3 Perform the analysis as described in steps 6.3.3 through 6.3.8.

6.4.4 Compare the recovery of the surrogates in the purgeable standard with that observed in the blank. Deviations of more than ± 30 percent from theoretical are an indication of a problem (e.g. leakage in the purge and trap device) that needs to be corrected before proceeding further.

6.4.5 Process the data from the purgeable standard and record the integrated area of the quantitation ion of each component as well as its retention time.

6.4.6 Repeat steps 6.4.2 through 6.4.5 with as many other volumes of the purgeable standard solution as are necessary to define the working range ofthe analytical system.

6.5 Sample analysis:

6.5.1 Allow the water sample to come to room temperature.

6.5.2 Remove the plunger from a 10-mL syringe and attach a closed syringe valve and needle. Open the sample vial and carefully pour the sample into the barrel of the syringe until it overflows. Replace the syringe plunger, open the syringe valve, and vent any air present. Adjust the plunger to the 10.0-mL mark. Add 10 µL of the surrogate/ internal standard solution. Close the syringe valve, and mix.

6.5.3 Transfer 5.0 mL of sample into a clean purge tube. Close the syringe valve and retain the second 5.0-mL aliquot of sample for future analysis, if needed. The second aliquot is preserved in this manner since the integrity of the original water sample is destroyed after it is opened.

6.5.4 Perform the analysis as described in steps 6.3.3 through 6.3.8.

6.5.5 Compare the recovery of the surrogates in the sample with that observed in the blank (step 6.3.8). If the recovery is not in the range of 70 to 130 percent, the sample should be reanalyzed.

6.5.6 Examine all of the mass spectral data from the sample. Identify analytes by a library search with a satisfactory match error. Positive identification is obtained when (1) the retention time is within 5 percent of the authentic material in the purgeable standard (step 6.4.5), and (2) three of the characteristic ions of the analyte maximize within ± 1 scan of each other.

6.5.7 Integrate and record the area under the quantitation ion for each analyte identified in step 6.5.6. If the areas are greater than the calibration range of the analytical system, the sample needs to be reanalyzed using a smaller volume of sample. It may be necessary to add additional internal standard for smaller sample volumes.

6.5.8 If very high levels of analytes or contaminants are found in a sample, analyze a blank to demonstrate no carryover.

7. Calculations

7.1 External standard method:

7.1.1 Calculate a response factor for an analyte (step 6.4.5) according to the equation

$$RF = \frac{A}{C \times V},$$

where
RF= response factor of analyte, in area/ng,
C = concentration of analyte in purgeable standard, in ng/µL,
V = volume of purgeable standard analyzed, in µL, and
A = area of quantitation ion of analyte.

7.1.2 Calculate the concentration of the analyte in the original water sample from the equation

$$Concentration(ug/L) = \frac{A_s}{V_s \times RF},$$

where
A_S = area of quantitation ion of analyte in sample,
V_s = volume of original water sample analyzed, in mL, and
RF= response factor of analyte, in area/ng.

7.1.3 Calculate the percent recovery of each surrogate added to the water sample from the equation

$$\text{Recovery}(percent) = \frac{A_1}{A_2} \times 100,$$

where
A_1= area of quantitation ion of surrogate in water sample, and
A_2 = area of quantitation ion of surrogate added to blank.

7.2 Internal standard method:

7.2.1 Calculate the response factor of an analyte (step 6.4.5) in the purgeable standard from the equation

$$RF = \frac{A_s}{C_s},$$

where
RF= response factor of analyte, in area/ng,
A_S = area of quantitation ion of analyte, and
C_S = amount of analyte in purgeable standard, in ng.

7.2.2 Calculate the response factor of the internal standard (step 6.4.5) in the purgeable standard from the equation

$$RFI = \frac{AI_1}{CI_1},$$

where
RFI = response factor of internal standard in purgeable standard, in area/ng,
AI_1, = area of quantitation ion of internal standard in. purgeable standard, and
CI_1, = amount of internal standard in surrogate and internal standard solution, in ng.

7.2.3 Calculate a relative response factor from the equation

$$RRF = \frac{RF}{RFI},$$

where
RRF= relative response factor of analyte,
RF = response factor of analyte determined (step 7.2.1), and
RFI=response factor of analyte internal standard determined (step 7.2.2).

7.2.4 Calculate the concentration of an analyte in the original water sample from the equation

$$Concentration(ug/L) = \frac{A \times CI_2}{RRF \times AI_2 \times V},$$

where
A = area of quantitation ion of analyte in analyzed sample,
CI_2 = amount of internal standard in surrogate solution, in ng,
RRF= relative response factor determined (step 7.2.3),
AI_2, = area of quantitation ion of internal standard in analyzed sample (step 6.5.9), and
V = volume of original water sample analyzed, in mL.

7.2.5 Calculate the percent recovery of each surrogate added to the water sample from the equation

$$\text{Recovery}(percent) = \frac{A_1}{A_2} \times 100,$$

where
A_1 = area of quantitation ion of surrogate added to water sample, and
A_2 = area of quantitation ion of surrogate added to blank.

8. Report

Report concentrations of purgeable organic compounds in water or water-suspended-sediment mixtures as follows: less than 3 µg/L, as "less than 3 µg/L"; 3.0 µg/L and above, two significant figures.

9. Precision

Precision data are not available.

Selected references

Goerlitz, D.F., 1976, Determination of volatile organohalides in water and treated sewage effluents: U.S. Geological Survey Open-File Report 76-610, 14 p.

U.S. Environmental Protection Agency, 1979, Purgeables—Method 624: Federal Register, v. 44, no. 233, p. 69532.