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Determination of Residues of 1,2-Dichloropropane, *cis*- and *trans*-1,3-Dichloropropene, and Trichloronitromethane in Water by Purge and Trap Extraction, Capillary Gas Chromatography and Mass Selective Detection

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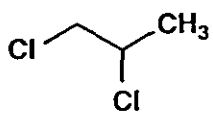
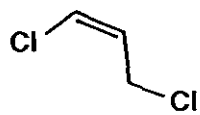
A. Scope

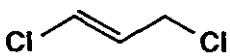
This method is applicable for the quantitative determination of residues of 1,2-dichloropropane (1,2-D), *cis*- and *trans*-1,3-dichloropropene (1,3-D), and trichloronitromethane (TCNM) in water over the concentration range of 0.05-40 ng/mL with a validated limit of quantitation of 0.05 ng/mL for each compound.



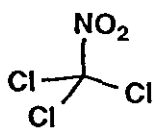
1,2-D
CAS No. 78-87-5



cis-1,3-D
CAS No. 10061-01-5



trans-1,3-D
CAS No. 10061-02-6



TCNM
CAS No. 76-06-2

B. Principle

This analytical method is based on established EPA purge and trap methodology for volatile organic analytes (VOAs) such as Method 524.2 (1). The volatile chlorinated hydrocarbons are purged from the water sample by sparging with helium, after which they are captured on a sorbent-containing trap. When purging is complete, the trap is heated and backflushed with helium, and the VOAs are desorbed and transferred to the injection port of a gas chromatograph (GC). The analytes are then separated on a capillary column and quantitated using mass selective detection (MSD).

C. Safety Precautions

1. Each analyst must be acquainted with the potential hazards of the reagents, products, and solvents used in this method before commencing laboratory work. SOURCES OF INFORMATION INCLUDE: MATERIAL SAFETY DATA SHEETS, LITERATURE, AND OTHER RELATED DATA. Safety information on non-DowElanco products should be obtained from the container label or from the supplier. Disposal of reagents, reactants, and solvents must be in compliance with local, state, and federal laws and regulations.
2. The analytes covered by this method, particularly TCNM, can cause severe and possibly fatal respiratory distress at air concentrations in the ppm range. All operations involving the neat analytes, or concentrated solutions of these compounds, must be carried out in a fume hood. In addition, the effluent from the GC split vent should be routed into an exhaust vent or through a carbon trap to prevent the release of the analytes into the laboratory air.

D. Equipment (Note N.1.)

1. Balance, analytical, Model AE200, Mettler Instrument Corporation, Hightstown, NJ 08520.
2. Gas chromatograph, Model 5890 Series II, Hewlett-Packard, Wilmington, DE 19808.
3. Mass selective detector, Model 5971, Hewlett-Packard, Palo Alto, CA 94304.
4. Mass selective detector data system, Model G1034B, Hewlett-Packard.
5. Purge and trap autosampler, Model 2016, Tekmar Company, Cincinnati, OH 45249.
6. Purge and trap concentrator, Model 3000, Tekmar Company.
7. Water purification system, Model Milli-Q UV Plus, Millipore Corporation, Milford, MA 01757.

E. Glassware and Materials (Note N.1.)

1. Column, capillary gas chromatography, DB-VRX, 30 m x 0.25 mm i.d., 1.4 µm film thickness, catalog number 122-1534, J&W Scientific, Folsom, CA 95630.
2. Column inlet liner, deactivated, double gooseneck, catalog number 5181-3315, Hewlett-Packard, Kennett Square, PA 19348.
3. Filter, charcoal, catalog number 7972, Chrompack, Inc., Raritan, NJ 08869. (Note N.2.)
4. Filter, moisture, catalog number 7971, Chrompack, Inc. (Note N.2.)
5. Filter, oxygen, catalog number 7970, Chrompack, Inc. (Note N.2.)
6. Flask, 40 mL volumetric, catalog number 042029-0801, Kontes, Vineland, NJ 08360.
7. Frit sparge glassware, 25 mL, catalog number 14-3022000, Tekmar Company.
8. Gas, helium, 99.995% purity, Airco, Murray Hill, NJ 07974.
9. Syringe, gas-tight, fixed needle, 10, 100, 500, and 1000 µL, catalog numbers 1701, 1710, 1750, and 1001, Hamilton Company, Reno, NV 89520.
10. Syringe, gas-tight, Luer Lock, 25 mL, catalog number 1025, Hamilton Company.

11. Syringe valve, catalog number 2-0940M, Supelco, Inc., Bellefonte, PA 16823.
12. Trap, Tenax, catalog number 12-0083-003, Tekmar Company.

F. Reagents and Chemicals (Note N.1.)

1. Reagents

a. Hydrochloric acid, concentrated, ACS reagent grade, catalog number A144-500, Fisher Scientific, Pittsburgh, PA 15219.

b. Internal standard, 2-bromo-1-chloropropane, 95%, compound number 23,127-4, Aldrich Chemical Company, Milwaukee, WI 53233.

c. Methyl alcohol, purge and trap grade, catalog number 41,481-6, Sigma-Aldrich, St. Louis, MO 63178.

d. Standards

(1) 1,2-dichloropropane

The 1,2-D standard used for generating the validation data contained in this method was Lot Number AGR277102, with a purity of 99.2%.

(2) *cis*-1,3-dichloropropene

The *cis*-1,3-D standard used for generating the validation data contained in this method was Lot Number AGR164301, with a purity of 97.1%.

(3) *trans*-1,3-dichloropropene

The *trans*-1,3-D standard used for generating the validation data contained in this method was Lot Number TSN100232, with a purity of 97.2%.

(4) trichloronitromethane

The TCNM standard used for generating the validation data contained in this method was Lot Number TSN100245, with a purity of 98.9%.

Obtain all standards from Test Substance Coordinator, DowElanco, Indianapolis, IN 46268-1053.

e. Water, distilled/deionized, purified using a Milli-Q UV Plus purification system (Section D.7.).

2. Prepared Solutions

Hydrochloric Acid, 1/1 (v/v):

Prepare by adding 100 mL concentrated HCl to 100 mL distilled/deionized water.

G. Preparation of Standards

1. Preparation of VOA Standard Solutions

NOTE: CARRY OUT THIS PROCEDURE IN A FUME HOOD. When mixing standard solutions, do not shake them excessively, as loss of analytes may occur. Mix by capping and gently inverting the solutions approximately five times. Store all standard solutions under frozen conditions in vials with PTFE-lined lids and screw-cap closures. Do not store samples and standards together in the same freezer. Allow standard solutions to warm to room temperature prior to use.

a. Tare a 100-mL volumetric flask containing approximately 80 mL of methanol. Add 0.1100-0.1300 g of 1,2-D dropwise via Pasteur pipette (approximately eight to ten drops). Make sure that the liquid falls directly into the methanol and does not run down the inside walls of the volumetric flask. Stopper the flask. Reweigh the flask and calculate the exact weight of the analyte added (Note N.3.). Bring the solution to volume with methanol to yield a stock solution of approximately 1.2 g/L 1,2-D. Calculate the exact concentration of the stock solution; if the standard is less than 97% pure, make the correction for percent purity as follows (A purity of 96% for the 1,2-D standard was assumed for the purpose of this example):

$$\frac{\text{1,2-D, g}}{\text{Total solution volume, L}} \times \frac{\text{\% purity}}{100} = \text{corrected concentration (g/L)}$$

$$\frac{0.1100 \text{ g 1,2-D}}{0.100 \text{ L}} \times \frac{96}{100} = 1.056 \text{ g/L}$$

b. Repeat step G.1.a. for *cis*-1,3-D, *trans*-1,3-D, and TCNM, preparing a stock solution of approximately 1.2 g/L for each analyte.

c. Using gas-tight syringes, transfer 1/C mL of each stock solution (where C = the concentration of the stock solution in g/L) into a single 100-mL volumetric flask containing approximately 80 mL of methanol. Dilute to volume with methanol to obtain a standard solution containing all four analytes, each at a concentration of 10.0 mg/L (or 10000 ng/mL). For example, a stock solution of 1.056 g/L 1,2-D would be diluted as follows:

$$1/1.056 \text{ g/L} = 0.947 \text{ mL} = 947 \text{ µL}$$

$$(947 \text{ µL})(1\text{x}10^{-6}\text{L/µL})(1.056 \text{ g/L})(1/100 \text{ mL}) = 0.00001 \text{ g/mL} = 10000 \text{ ng/mL}$$

d. Transfer 10.0 mL of the 10000 ng/mL standard solution into a 100-mL volumetric flask. Dilute to volume with methanol to obtain a standard solution containing all four analytes each at a concentration of 1000 ng/mL.

2. Preparation of the Internal Standard

a. Following the procedure outlined above in Sections G.1.a. and c., prepare a 10 mg/L solution of the internal standard, 2-bromo-1-chloropropane. (It is not necessary to correct for percent purity of the internal standard.)

b. Transfer 10.0 mL of the 10 mg/L internal standard solution to a 40-mL volumetric flask and dilute to volume with methanol to obtain a 2.50 mg/L internal standard solution.

3. Preparation of the Calibration Standard Solutions

Prepare aqueous calibration standards of the VOAs by transferring aliquots of the standard solutions (Sections G.1.-2.) into the appropriate volumetric flasks containing distilled/deionized water, as outlined below. Use an appropriately-sized gas-tight syringe to transfer the standard solution and inject it into the water below the narrow neck of the flask. **Because aqueous solutions of VOAs are not stable in any container with headspace, each calibration standard should be prepared just prior to purge and trap analysis.**

a. Low range calibration standard solutions (Section J.1.):

Aliquot of 1000 ng/mL Standard Soln.[a]	Final Calibration Std. Volume	Calibration Std. Final Conc.	Equivalent Sample Conc.[b]
µL	mL	ng/mL	ng/mL
5.00	200	0.0250	0.0250
5.00	100	0.0500	0.0500
10.0	100	0.100	0.100
25.0	100	0.250	0.250
50.0	100	0.500	0.500
100.0	100	1.00	1.00

[a] Section G.1.d.

[b] The concentration in an aqueous calibration standard directly corresponds to the same concentration in a field sample, unless the sample has been diluted prior to analysis.

Transfer a 5.0-µL aliquot of the 10.0 mg/L internal standard solution (Section G.2.a.) to each calibration standard (with the exception of the 0.025 ng/mL standard, which requires 10.0 µL of internal standard as a result of its final volume) to obtain an internal standard concentration of 0.500 ng/mL.

b. High range calibration standard solutions (Section J.1.):

Aliquot of 10000 ng/mL Standard Soln.[a]	Final Calibration Std. Volume	Calibration Std. Final Conc.	Equivalent Sample Conc.[b]
µL	mL	ng/mL	ng/mL
10.0	100	1.00	1.00
20.0	100	2.00	2.00
40.0	100	4.00	4.00
100.0	100	10.0	10.0
200.0	100	20.0	20.0
400.0	100	40.0	40.0

[a] Section G.1.c.

[b] The concentration in an aqueous calibration standard directly corresponds to the same concentration in a field sample unless the sample has been diluted prior to analysis.

Transfer a 50.0-µL aliquot of the 10.0 mg/L internal standard solution (Section G.2.a.) to each calibration standard to obtain an internal standard concentration of 5.00 ng/mL.

H. Purge and Trap

1. Purge and Trap Concentrator

Install the Tenax trap (Section E.12.) and sparge glassware (Section E.7.) on the Tekmar purge and trap concentrator (Section D.6) and autosampler (Section D.5.) following the manufacturer's recommended procedure.

2. Typical Operating Conditions

Instrumentation:	Tekmar 3000 Concentrator Tekmar 2016 Autosampler
Purge/Carrier Gas:	helium
Purge Flow	40 mL/min
Desorb Flow	20 mL/min
Trap Pressure	5 psi
Tekmar Controller Menu Settings:	
3000 Transfer Line	140 °C
3000 Valve	140 °C
2016 Transfer Line	130 °C
2016 Valve	130 °C
Moisture control system temp.	130 °C
Trap purge ready temp.	30 °C
Trap purge temp. setting	20 °C (i.e., not heated above ambient temp. during purge)
Sample heater	Off
Prepurge	0.00 min
Preheat time	0.00 min
Purge time	11.00 min
Dry purge time	2.00 min
Moisture control system desorb temp.	50 °C
GC Start	Desorb start
Cryo Focuser	Not applicable
GC cycle time	23 min
Desorb preheat	170 °C
Desorb time	2.00 min
Desorb temp.	180 °C
Sample drain	off
Bake time	10 min
Bake temp.	185 °C
Bake gas bypass	On
Bake gas bypass delay	2.00 min
Moisture control system bake	180 °C

I. Gas Chromatography/Mass Spectrometry

1. Column (Note N.4.)

Install the column inlet liner (Section E.2.) and the capillary column (Section E.1.) in the split/splitless injection port of the gas chromatograph/mass spectrometer (GC/MSD) following the manufacturer's recommended procedure.

2. Typical Operating Conditions

Instrumentation:	Hewlett-Packard Model 5890 Series II GC Hewlett-Packard Model 5971 Mass Selective Detector Hewlett-Packard Model G1034B Data System Software
Column:	J&W Scientific fused silica capillary DB-VRX liquid phase 30 m x 0.25 mm i.d. 1.4 µm film thickness
Temperatures:	
Column	35 °C for 1.0 min 35 °C to 140 °C at 9 °C/min 140 °C for 0.10 min 140 °C to 210 °C at 20 °C/min 210 °C for 2.0 min
Injector Interface	200 °C 230 °C
Carrier Gas:	helium
Head Pressure Linear Velocity	6 psi approximately 30 cm/sec @ 35 °C
Injection Mode:	Split (Note N.4.)
Splitter Flow Septum Purge	20 mL/min Off (capped)
Detector:	electron impact selected ion monitoring
Calibration Program Electron Multiplier	midmass autotune (Note N.5.) 1600 volts

Ions Monitored:

Compound	*m/z*, Quantitation	*m/z*, Confirmation
1,2-D	63	76
cis-1,3-D	75	112
trans-1,3-D	75	112
TCNM	119	82
2-bromo-1-chloropropane	77	–

Dwell Time: 75 msec

Full scan mass spectra of the above analytes and the internal standard are shown in Figures 1-5.

3. Typical Chromatograms

Typical chromatograms of a standard, control sample, and a 0.0500 ng/mL recovery sample for water are illustrated in Figures 6-17.

J. Calibration

1. General Approach

Because of the wide range of standard concentrations (0.0250-40.0 ng/mL) used in this method, it is unlikely that any single calibration curve will provide accurate quantitation over the entire range. In general, deviations from the calculated curve will be most severe at the low end of the curve, which affects measurements near the LOQ. To improve quantitation, it is useful to divide the calibration range into two subranges and to produce a separate calibration curve for each. Thus, the low range will encompass VOA concentrations of 0.0250-1.00 ng/mL, and the high range 1.00-40.0 ng/mL.

A calibration check (Section J.4.) must be carried out at the beginning of each twelve-hour period during which samples are analyzed in order to confirm calibration of the instrumentation.

2. Initial Calibration

a. Prior to analyzing any standards, bake out the trap at approximately 185 °C and set the GC oven temperature to 220 °C for 10 minutes.

b. Select either the low or high range for calibration. After the system has been returned to its starting conditions, load the first aqueous calibration standard (Section G.3.) in the selected range by removing the plunger from the 25-mL gas-tight Luer Lock syringe (Section E.10.), attaching the closed syringe valve (Section E.11.) to the Luer lock, and pouring the standard into the open end of the syringe until it is nearly full. (Do not draw the standard up into the syringe.) Replace the syringe plunger in the barrel, open the valve, expel any air from the syringe, and adjust the volume to exactly 25.0 mL. Open the loading valve on the purge and trap device and load the standard into the sparge tube. Analyze the standard by purge and trap using GC/MSD as described in Sections H. and I.

c. Repeat J.2.b. for each standard in the calibration range. After each standard has been analyzed, rinse the sparge tube with two approximately 25-mL aliquots of distilled/deionized water before loading the next standard. Standards should always be analyzed from lowest to highest concentration to minimize carryover. (Note N.6.)

3. Calibration Curve

a. Following analysis of the range of calibration standards described in G.3.a. (low range) or G.3.b. (high range), determine the peak areas for 1,2-D (*m/z* 63), *cis*-1,3-D (*m/z* 75), *trans*-1,3-D (*m/z* 75), TCNM (*m/z* 119), and 2-bromo-1-chloropropane (IS) (*m/z* 77).

b. For each analyte, prepare a standard curve by plotting the concentration (ng/mL) on the abscissa (x-axis) and the standard/IS peak area ratio (Quantitation Ratio) on the ordinate (y-axis) as shown in Figures 18-21. Using regression analysis, determine the equation for the curve with respect to the abscissa.

For example, using power regression (2) with the 1,2-D data from Figure 18:

$$Y = \text{constant} \times X^{(\text{exponent})}$$

Solving for X:

$$X = \left(\frac{Y}{\text{constant}}\right)^{1/\text{exponent}}$$

where: X = concentration (ng/mL), Y = Quantitation Ratio

$$\text{1,2-D Conc. ng/mL} = \left(\frac{\text{Quantitation Ratio}}{\text{constant}}\right)^{(1/\text{exponent})}$$

$$\text{1,2-D Conc. ng/mL} = \left(\frac{\text{Quantitation Ratio}}{1.37594}\right)^{(1/1.04500)}$$

c. Typical calibration curves for the determination of each of the analytes in water are shown in Figures 18-21.

4. Calibration Check

a. For the low calibration range, prepare a 0.100 ng/mL calibration standard (Section G.3.a.); for the high range, prepare a 2.00 ng/mL calibration standard (Section G.3.b.).

b. Analyze the calibration check standard and calculate the amount of each analyte present, using the equation for the current calibration curve for each analyte. (Section J.3.)

c. Calculate the absolute value of the percent difference in the calculated and the theoretical standard concentration as follows:

$$|(1 - (\text{Calculated}/\text{Theoretical}))| \times 100$$

If the difference in the calculated and theoretical value for each analyte in the calibration check standard is less than 10%, the existing curves are considered to be valid. Sample analysis may proceed.

d. If the difference in the calculated and theoretical value for any analyte exceeds 10%, the original calibration is no longer considered valid, and a new initial calibration (Section J.2.) must be carried out prior to continuing with sample analysis. A new initial calibration must always be carried out for all analytes prior to sample analysis whenever major maintenance (column change, source cleaning, filament or multiplier replacement, trap replacement, etc.) is performed on the purge and trap GC/MSD system. Minor maintenance (replacing GC septum or inlet liner, removing a portion of the upper end of the column, etc.) does not automatically necessitate recalibration, but must be examined on a case-by-case basis.

K. Determination of Recovery of 1,2-D, *cis*-1,3-D, *trans*-1,3-D, and TCNM in Water

1. Preparation of Recovery Samples

   a. Following analysis of the last calibration standard or check standard, rinse the sample sparge tube(s) twice with distilled/deionized water and analyze a reagent blank consisting of 25.0 mL distilled/deionized water. Pour the water into the open barrel of the Luer Lock syringe with attached syringe valve, and adjust the volume to 25.0 mL (Section J.2.b.). Remove the syringe valve, pull the plunger back slightly, and inject 5.0 µL of the 2.5 mg/L internal standard (Section G.2.b.) through the Luer Lock tip into the sample, if the analyses are being conducted in the low-level calibration range. If the analyses are being conducted in the high-level calibration range, add 50.0 µL of the 2.5 mg/L internal standard to the sample in the same manner. Load the sample into the sparge tube and begin the analysis. Calculate the levels of analytes detected (Section J.3.). If the concentration of any analyte exceeds 30% of the targeted limit of quantitation for the analysis (Section M.1.c.), additional blanks should be run until a "clean" blank is obtained.

   b. Obtain a control sample of ground or surface water from the field sampling location. Analyze an aliquot of the control (Section K.1.a.) to demonstrate that none of the analytes of interest are detectable in the control sample.

   c. Prepare fortified samples at appropriate concentrations over the range of 0.050-40.0 ng/mL as described in Section G.3. for the standards, using the natural ground or surface water instead of distilled/deionized water.

      It may be necessary to preserve natural water samples with 1/1 HCL (Section F.2.) (two drops per mL) if bacteria are present that degrade the specific analytes of interest. (Note N.7.)

   d. Analyze the fortified recovery samples by purge and trap using GC/MSD as described in Sections H. and I.

2. Calculation of Percent Recovery

   a. Determine the peak areas for 1,2-D (*m/z* 63, 76), *cis*-1,3-D (*m/z* 75, 112), *trans*-1,3-D (*m/z* 75, 112), TCNM (*m/z* 119, 82), and IS (*m/z* 77) for each calibration standard analyzed as part of the current calibration curve (Section J.2.).

   b. For each standard, calculate the confirmation ratio for each of the four analytes. The average confirmation ratio for each analyte will be used to confirm the presence of that analyte in the water samples.

      For example, using the data for 1,2-D from Figure 6:

$$\text{Confirmation Ratio} = \frac{\text{peak area of quantitation ion}}{\text{peak area confirmation ion}}$$

$$\text{Confirmation Ratio} = \frac{\text{peak area } mz\ 63}{\text{peak area } mz\ 76}$$

$$\text{Confirmation Ratio} = \frac{1415}{511}$$

$$\text{Confirmation Ratio} = 2.77$$

Positive confirmation of the presence of each analyte is indicated when the confirmation ratio for the samples is in the range of ± 15% of the average found for the standards in the current calibration curve.

c. Prepare a standard curve for each of the analytes and determine the equations for the calibration curves using regression analysis as described in J.3.

d. Determine the net concentration of 1,2-D in each recovery sample by first subtracting the average quantitation ratio of the control samples from that of the recovery sample. Substitute the net quantitation ratio obtained into the calibration curve equation and solve for the concentration.

For example, using power regression and the 1,2-D data from Figures 10, 14, and 18:

$$\text{1,2-D Conc. (ng/mL)} = \left(\frac{\text{(net quantitation ratio)}}{1.37594}\right)^{1/1.0450}$$

$$\text{1,2-D Conc. (ng/mL)} = \left(\frac{(0.0673)}{1.37594}\right)^{1/1.0450}$$

$$\text{1,2-D Conc.} = 0.0557 \text{ ng/mL}$$

e. Determine the percent recovery by dividing the concentration found for each recovery sample by the theoretical concentration added.

$$\text{Recovery} = \frac{\text{Concentration Found}}{\text{Concentration Added}} \times 100\%$$

$$\text{Recovery} = \frac{0.0557 \text{ ng/mL}}{0.0500 \text{ ng/mL}} \times 100$$

$$\text{Recovery} = 111\%$$

f. For each analyte, determine the concentration found and corresponding percent recovery as described for 1,2-D in Section K.2.d.-e.

The average recovery for each analyte in a given sample set will be used to correct for daily method efficiency.

L. Determination of VOAs in Water

1. Calibrate the instrument/check calibration over the appropriate calibration range for the sample set as described in Section J.

2. Prepare and analyze reagent blanks, controls, and recovery samples as described in Section K.1. Rinse the sample sparge tube(s) between samples with distilled/deionized water. If standards or recovery samples spiked at 1.00 ng/mL or higher were analyzed prior to initiating the analysis of a set of water samples, analyze a blank in that sparge tube as in section K.1.a. in order to ensure that carryover is not a problem.

3. Allow the field samples to warm to room temperature. Examine the sample vials for headspace; any sample contained in a vial which is not completely full (free of air bubbles) is an invalid sample and should be discarded.

4. If it is anticipated that the concentration is likely to exceed the upper limit of the calibration range, the water sample should be diluted with distilled/deionized water by an appropriate factor prior to analysis. If the concentration of analytes in a group of samples is unknown, a 1:100 dilution of at least one of the samples should be analyzed first to estimate the sample concentration and prevent contaminating the instrument with a very high-level sample. (Note N.8.)

5. Load a sample into a gas-tight syringe as in Section K.1.a. After the sample volume has been adjusted to exactly 25.0 mL, transfer 5 µL (for the low calibration range) or 50.0 µL (for the high calibration range) of the 2.5 mg/L internal standard solution into the sample using a gas-tight syringe. Add the internal standard solution by removing the syringe valve, pulling the plunger back slightly, and injecting the internal standard through the Luer-Lock tip.

6. Open the loading valve on the purge and trap device and transfer the sample into the sparge tube. Analyze the sample by purge and trap using GC/MSD as described in Sections H. and I. (The purge and trap autosampler permits the loading and subsequent automated analysis of a set of 16 samples.

7. Determine the concentration of each volatile analyte of interest by substituting the quantitation ratio into the equation for the corresponding standard calibration curve (Section J.3.), calculating the uncorrected (gross) result.

   For example, using the 1,2-D data from Figures 14 and 18, the uncorrected concentration is calculated as follows:

$$\text{1,2-D Conc. (ng/mL)} = \left(\frac{\text{(1,2-D quantitation ratio)}}{1.37594}\right)^{1/1.0450} \text{ x any dilution factor}$$

$$\text{1,2-D Conc. (ng/mL)} = \left(\frac{0.0673}{1.37594}\right)^{1/1.0450} \text{ x any dilution factor}$$

$$\text{1,2-D Conc. (ng/mL)} = 0.0557 \times 1$$

$$\text{1,2-D Conc.} = 0.0557 \text{ ng/mL}$$

8. The uncorrected results as determined in section L.7. must be reported. In addition, the results can be corrected for method recovery using the following procedure:

   a. Calculate the mean % recovery of each analyte for the recovery samples analyzed with the treated samples on the same day.

   b. Determine the corrected analyte concentration in the water samples as follows (Assume a mean % recovery for 1,2-D of 105 for the purpose of this example.):

$$\text{1,2-D Conc. (corrected ng/mL)} = \frac{\text{uncorrected 1,2-D (ng/mL) x 100}}{\text{\% Recovery}}$$

$$\text{1,2 - D Conc. (corrected ng/mL)} = \frac{0.0557 \times 100}{105} = 0.0530$$

9. When analyzing samples using a high range calibration, any sample giving a peak area ratio response for one or more of the analytes which is greater than 10 percent below that of the lowest standard in the current calibration curve must be reanalyzed using the low level calibration range (Section G.3.a.). Any sample giving a peak area ratio response greater than 10 percent above that of the highest standard in the current calibration curve must be reanalyzed, following appropriate dilution of the sample with distilled/deionized water to bring it within the calibration range. (Note N.8.) The additional dilution must then be accounted for in the calculation of the result (Section L.7.).

3. Assay Time

A typical analytical run would consist of a minimum of six calibration standards encompassing the expected range of sample concentrations, a reagent blank, a control (a non-fortified sample), a minimum of two fortified controls (one of which must be at the target LOQ), and sixteen samples. This typical analytical run could be prepared in approximately 8 hours, with the purge and trap/chromatographic analysis continuing into the same evening.

As indicated in Section J., once the instrument has been calibrated, a calibration check can be done every twelve hours by analyzing a single standard to verify that the existing calibration curve is still valid. This reduces the amount of time required for daily calibration, and allows the analysis of a greater number of samples per day.

N. Notes

1. Equipment, glassware, materials, reagents, and chemicals considered to be equivalent to those specified may be substituted with the understanding that their performance must be confirmed by appropriate tests. Common laboratory supplies are assumed to be readily available and are, therefore, not listed.
2. The filters are used in the carrier gas supply lines to purify the helium entering the gas chromatograph and sparging apparatus.
3. An alternate method for transferring the neat standards to the methanol contained in the volumetric flask is to tare a gas-tight syringe, draw an amount of the neat standard into the syringe, reweigh the syringe determining the weight of the standard, and transfer the standard from the syringe to the flask by injecting it below the surface of the methanol contained in the flask. Rinse the syringe into the flask to be certain that the analyte contained in the syringe is completely transferred to the flask.
4. The purge and trap concentrator is interfaced with the gas chromatograph by cutting the GC helium inlet line approximately 4 cm from its entry into the injection port. The cut end of the helium line is routed to the concentrator, and the concentrator's transfer line is connected to the remaining short section of tubing leading to the injector. The flow from the purge and trap concentrator is 20 mL/minute and the flow through the column is approximately 1 mL/minute; therefore, a 19:1 split will occur. The injector should be run in the split mode at all times. While this technique appears to sacrifice sensitivity by splitting off 95% of the analytes, it permits the use of normal-dimension capillary columns (0.18 or 0.25 mm i.d.) rather than megabore columns which necessitate the use of jet separators or cryogenic interfaces at the GC/MSD. By virtue of the superior resolution possible with the 0.25 mm i.d. capillary column, the desired limits of quantitation (0.0500 ng/mL) are readily attained for all analytes.

5. The mass spectrometer should be tuned prior to analysis of a set of calibration standards and generation of a calibration curve. Once the instrument has been calibrated it should not be tuned again until just prior to analysis of a fresh set of calibration standards for generation of a new calibration curve.
6. It is possible to load all standards in a calibration curve onto the Tekmar 2016 autosampler prior to beginning the analysis; however, this then requires rinsing of all sparge tubes used and confirming the absence of carryover prior to analyzing samples. Using a single sparge tube to analyze consecutively loaded standards confines the potential for contamination and need for cleaning to a single tube.
7. Over the course of developing this method, it was discovered that levels of TCNM in distilled/deionized water were stable at room temperature for several hours; however, equal levels in natural surface water decreased rapidly. This was attributed to bacterial degradation and preservation by acidification of the surface water samples to approximately pH 2 stopped the loss of the analyte. (No degradation was observed for the other three analytes in surface water, either acidified or unacidified.) Surface water from any test site should be evaluated to determine the need for preservation prior to collection of the field samples. If necessary, acidification must be done at the time of sample collection for field samples, and at the time of fortification for calibration standards and recovery samples.
8. Following removal of an aliquot for analysis from a sample vial, the remaining sample is no longer valid due to the presence of headspace in the vial. As a result, any time a sample must be reanalyzed, the aliquot for reanalysis must be taken from a sealed replicate of the initial sample.