DETERMINATION OF 1,2,3-TRICHLOROPROPANE IN DRINKING WATER BY PURGE AND TRAP GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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1. Scope and Application

1.1. This method may be used to determine 1,2,3-trichloropropane (TCP), CAS No. 96-18-4, in water at concentrations below the quantifiable ranges of USEPA methods 504.1, 551.1 and 524.2.

1.2. The linear calibration range for TCP is from 5.0 to at least 500 ng/L. Higher concentrations of TCP have not been tested, as the purpose of this method is trace-level analysis. As a general guide, use methods 504.1 or 551.1 for TCP concentrations =100 ng/L and method 524.2 for TCP concentrations =500 ng/L.

1.3. Although similar to USEPA method 524.2, this single analyte method is designed to quantitate TCP at concentrations as low as 5 ng/L. Both the quadrupole mass spectrometer (MS) and the ion trap MS detectors were used in the development of this method. (See Table 1.) To achieve the required sensitivity, the quadrupole MS was operated in the selected ion monitoring (SIM) mode, while the ion trap MS was operated in the selected ion storage (SIS) mode. Under the conditions described in this method, the quadrupole MS achieved better sensitivity than the ion trap MS. Ion trap users are cautioned that quantifying TCP at the 5 ng/L level may not be achievable. (See Section 12 for performance.) However, when using the detector parameters described in this method, the ion trap MS in the SIS mode will generate a "spectrum" that provides better identity confirmation than the quadrupole MS in the SIM mode.

1.4. The applicable matrices include drinking water, ground water and surface water. Although not specifically tested, this method should also be applicable to wastewaters.

1.5. This method is recommended for use by analysts experienced in gas chromatography/mass spectrometry (GC/MS) and in the interpretation of the resulting ion chromatograms and mass spectra. Analysts using this method should also be proficient in using method 524.2

1.6. Disclaimer: Mention of trade names or commercial products in this method does not constitute endorsement or exclusive recommendation for use. Laboratories may make equivalent product substitutions.

2. Summary of Method

2.1. The analysis is performed using purge and trap and GC/MS. TCP is identified by matching the retention time and fragment ions from the sample with those of the reference standard. Quantitation is performed by the isotopic dilution procedure. 1,2,3-trichloropropane-D_5 (TCP- D_5) is used as the internal standard, which is added at the same concentration to the samples and standards.

3. Interferences

3.1. Ensure that all solvents, reagents, glassware, and equipment used in the analysis are free from interfering contaminants.

3.2. Volatile organic compounds which coelute or overlap with TCP or TCP-D5 and which yield the same fragment ions as TCP or TCP-D5 can be a major source of error. Due

to the extreme sensitivity of this method, even low abundances of these ions can result in severe interference when the interfering compound is present at sufficiently high concentration. Under the conditions described in this method, the following compounds have the potential to interfere.

3.2.1. DB-VRX column: The high abundance m/z 75 ion from *trans*-1,4-dichloro-2-butene, interferes with the TCP m/z 75 quantitation ion, if the two compounds overlap. The low abundance m/z 79 ion from *o*-xylene interferes with the TCP-D_5 m/z 79 quantitation ion, if o-xylene is present at high concentration and overlapping occurs.

3.2.2. DB-5.625 column: At high concentration, the m/z 75 ion from isopropyl benzene interferes with the TCP m/z 75 quantitation ion, if overlapping occurs.

4. Safety

4.1. Observe the safety precautions as described in method 524.2

5. Equipment and Supplies

5.1. Purge and trap concentrator system: Same as the system described in method 524.2. However, the system should be equipped with the following.

5.1.1. 25 mL fritted glass sparger, moisture control device, and heating mantle or similar device to allow heating of the sample in the sparger glassware to 40°C.

5.1.2. The Vocarb 3000 trap (Supelco) was used in the development of this method, but other traps with equivalent performance may be substituted.

5.2. Gas chromatograph: Same as described in method 524.2.

5.2.1. Capillary GC columns used in the development of this method:

5.2.1.1. 30-meter x 0.25 mm DB-5.625 with a 1.0 µm film thickness (J&W Scientific).

5.2.1.2. 60-meter x 0.25 mm DB-VRX with a 1.4 µm film thickness (J&W Scientific).

5.2.1.3. An alternate column may be used if it provides the required separation and performance for this method.

5.3. Mass spectrometer and data system: Same as described in method 524.2, except the mass spectrometer and data system must be capable of the following.

5.3.1. Quadrupole mass spectrometer: Must be capable of operating in the selected ion mode (SIM).

5.3.2. Ion trap mass spectrometer: Must be capable of operating in the selected ion storage mode (SIS).

5.4. Sample containers: 40 mL amber VOA vials with screwcaps containing a PTFE- faced silicone septums. The vials may be purchased as pre-cleaned, level 2.

5.5. Assorted glass micro-syringes for preparing standards and fortification solutions.

5.6. Assorted volumetric flasks and vials with PTFE- lined screwcaps for standards preparation and storage.

6. Reagents and Standards

6.1. Reagent water: Boiled and free from TCP and other interfering contaminants.

6.2. Methanol: Purge and trap grade.

6.3. Primary standard: 1,2,3-Trichloropropane, 5000 µg/mL in methanol (Supelco, or equivalent). Prepare a working stock solution and a primary dilution standard in

methanol. Use the primary dilution standard to prepare the aqueous calibration standards at the concentrations of 5.0, 10, 20, 50, 100 ng/L, or higher, as required.

6.4. Labeled internal standard: 1,2,3-Trichloropropane-D_5, 98% (Cambridge Isotopes, or equivalent). Ensure that the TCP-D_5 standard contains less than 0.5% of the native compound (TCP). Prepare a working stock solution and a primary dilution standard in methanol. Spike all prepared standards, samples, and blanks with the primary dilution standard before conducting the analysis. It is recommended that the internal standard concentration in the aqueous working samples should not exceed 50 ng/L.

7. Sample Collection, Preservation and Storage

7.1. Collect samples in duplicate in 40 mL amber VOA vials as described in method 524.2.

7.2. If the samples contain residual chlorine, add 25 mg of ascorbic acid to each vial before sample collection.

7.3. Store samples at 4°C until analysis. Protect from direct sunlight or other bright light sources. The sample storage area must be free from organic solvent vapors.

7.4. All samples must be analyzed within 14 days of collection.

8. Quality Control

8.1. An initial demonstration of capability

8.1.1. Prepare and analyze a laboratory reagent blank (LRB) to demonstrate that the preparation procedures, glassware, reagents and instrument system are free from interfering contaminants.

8.1.2. Prepare and analyze seven replicates of a laboratory fortified blank (LFB) containing TCP in the range of 20 to 50 ng/L. The mean recovery should be within 80-120% and the relative standard deviation (RSD) should be =20%.

8.1.3. Perform a method detection limit (MDL) study by preparing and analyzing a minimum of seven replicates of a 5.0 ng/L TCP standard over a period of three days, or more. Calculate the MDL as follows.

MDL = the product of S and $t_{(n-1,\ 1-a=0.99)}$

where: S = standard deviation of the replicate analysis.
t = Student's t value for the 99% confidence level with n-1 degrees of freedom.
n = number of replicates.

8.1.4. The reporting level should be no less than three times the MDL. A TCP reporting level of 5.0 ng/L requires a MDL of 1.7 ng/L, or less.

8.2. Assessing laboratory performance

8.2.1. Before processing samples, a LRB must be analyzed to demonstrate that all glassware and reagents are free of interfering contaminants. A LRB must be analyzed with each batch of samples of 10 samples, or less, or when reagents are changed. LRB results should be non-detects (< MDL).

8.2.2. Each day that samples are analyzed, a LFB must be analyzed with each batch of 10 samples, or less. For the GC/MS-quadrupole system, prepare the LFB

with a TCP concentration of 5.0 ng/L. For GC/MS-the ion trap system, prepare the LFB with a TCP concentration of 10 ng/L. The LFB recovery should be within the range of 80- 120% of the fortified concentration.

8.2.3. In addition, the integrated areas of the TCP-D_5 responses should be monitored during the day, as another check on system sensitivity. (See Section 9.5.3.)

8.2.4. Analyze at least one sample in duplicate per batch of 10 samples, or less.

8.2.5. At least quarterly, analyze a TCP quality control sample from an external source to assess laboratory performance.

9. Calibration and Standardization

9.1. Calibrate the instrument by analyzing a minimum of five calibration standards in the range of
5.0 to 100 ng/L, or higher, as required.

9.2. The capillary columns and temperature programs listed in Table 1 provide sufficient separation between TCP and TCP-D_5. In addition, the two compounds do not interfere with each other's quantitation ion. Since corrections to isotopic abundances are not required when calculating the isotope ratio of TCP to TCP-D_5, a response factor (similar to the internal standard response factor calculation) for TCP may be calculated as follows.

RF is equal to the product of A_{TCP} and $Q_{TCP\ -D5}$ divided by the product of $A_{TCP\ -D5}$ and Q_{TCP}

where: A_{TCP} = integrated abundance of the m/z 75 quantitation ion for TCP.
$A_{TCP\ -D5}$ = integrated abundance of the m/z 79 quantitation ion for the internal standard, TCP-D_5.
Q_{TCP} = concentration of TCP in ng/L.
$Q_{TCP\ -D5}$ = concentration of the internal standard, TCP-D_5, in ng/L.

9.3. Calculate the mean response factor (RF_{mean}) and standard deviation of the five concentration levels. If the RSD for the initial calibration exceeds 20%, check for linearity and recalibrate.

9.4. As an alternative to calculating the mean response factor, a linear regression curve may be generated from the initial calibration data by plotting the ratio of $A_{TCP}/A_{TCP\ -D5}$ versus Q_{TCP}.

9.5. For continuing calibration, verify the calibration by analyzing a midpoint calibration standard during the course of sample analysis. The RF should be within 20% of RF_{mean} from the initial calibration, or within 20% of the true concentration if the calibration was performed by linear regression. If the RF or measured concentration exceeds 20%, a fresh standard should be prepared and then rerun. If the RF or measured concentration still exceeds 20%, a new calibration curve should be prepared.

9.5.1. Each set of samples must be bracketed by a calibration check standard or LFB.

9.5.2. During the continuing calibration, verify that the retention times have not drifted from those set in the initial calibration.

9.5.3. The absolute area of the quantitation ion of the TCP-D_5 in the LRB, LFB, and continuing calibration check standard should not have decreased by more than

20% from the initial calibration. If necessary, make appropriate adjustments to restore system sensitivity.

10. Procedure

10.1. See Table 1 for the instruments and instrument parameters that were used in the development of this method.

10.2. Bake out the trap on the purge and trap concentrator for 10 minutes before analyzing any standards or samples.

10.3. Prepare a 25 mL sample aliquot for analysis as in method 524.2, but use TCP-D_5 as the internal standard.

10.4. Analyze the sample as in method 524.2 using the instrument parameters from Table 1 in this method. The instrument parameters in Table 1 should be used as guidelines.

10.5. TCP is identified by matching the retention time and fragment ions and ion abundances from the sample with those of the reference standard. Identification requires expert judgment, especially when sample components are not completely resolved, or if TCP is present at very low concentration (near the detection limit). Background ions or interfering ions from coeluting compounds may make identification (and quantitation) difficult to achieve.

10.5.1. Quadrupole MS: Calculate the mean abundance ratio of the m/z 75 ion to the m/z 110 ion of TCP from the initial calibration data. Calculate and compare the abundance ratio of the sample with the reference mean value. The abundance ratio of the sample should compare within ±30% of the reference mean value.

10.5.2. Ion trap MS: Compare with the “spectrum” of the sample (m/z ranges 74 to 82, 96 to 104 and 109 to 116) with the “spectrum” of the reference standard. Care should be exercised when performing the comparison, as the SIS “spectrum” is composed of three discontinuous “m/z windows” and does not represent the complete spectrum.

10.6. Monitor the absolute area of the m/z 79 quantitation ion of the TCP-D_5 in samples. A significant increase in area may signify the additive effect of a m/z 79 ion from a coeluting compound.

10.6.1. If using the ion trap MS detector, compare the TCP-D_5 sample “spectrum” with the “spectrum” of the reference standard to help determine if any interfering compound may be present. The TCP-D_5 peak shapes in the extracted ion current profile (EICP) and the total ion current profile (TIC) should also be examined for possible coeluters.

10.6.2. If using the quadrupole MS detector and only the m/z 79 quantitation ion was measured for TCP-D5, examine the TCP-D_5 peak shapes in the EICP and the TIC for possible coeluters, or perform a sample matrix spike (a high TCP-D_5 response due to contribution from an interfering compound will result in a calculated TCP spike recovery that will be lower than normal).

10.6.3. Take appropriate corrective action, as necessary, to correct for interfering compounds.

11. Analysis and Calculations

11.1. Calculate the TCP sample concentration, using the multipoint calibration established in Section 9.

C_{TCP} is equal to the product of A_{TCP} and $Q_{TCP\ -D}5$ divided by the product of $A_{TCP\ -D_5}$ and RF_{mean}

Where: C_{TCP} = concentration of TCP in ng/L in the water sample

A_{TCP} = integrated abundance of the m/z 75 quantitation ion for TCP.
$A_{TCP\ -D_5}$ = integrated abundance of the m/z 79 quantitation ion for the internal Standard, TCP-D_5.
$Q_{TCP\ -D_5}$ = concentration of the internal standard, TCP-D_5, in ng/L.
RF_{mean} = mean response factor of analyte from the initial calibration.

11.2. Alternatively, the TCP sample concentration may be computed from the linear regression line established in Section 9.

12. Method Performance

12.1. GC/MS-quadrupole (System 1 in Table 1): Single laboratory, single operator.
- 12.1.1. A MDL study (n=7) conducted over a period of three days using reagent water fortified with 5.0 ng/L of TCP resulted in a calculated MDL of 0.9 ng/L. The mean recovery and relative standard deviation were 104% and 5.6%, respectively.
- 12.1.2. The estimated reporting limit was 5.0 ng/L.
- 12.1.3. The mean recovery and relative standard deviation for LFB samples (n=8) containing 50.0 ng/L of TCP were 97% and 4.2%, respectively.

12.2. GC/MS- ion trap (System 2 in Table 1): Single laboratory, single operator performance (lab and operator different from 12.1).
- 12.2.1. A MDL study (n=8) conducted over a period of three days using reagent water fortified with 5.0 ng/L of TCP resulted in a calculated MDL of 2.3 ng/L. The mean recovery and relative standard deviation were 101% and 15%, respectively.
- 12.2.2. The estimated reporting limit was 10 ng/L.
- 12.2.3. The mean recovery and relative standard deviation for QC samples (n=18) containing 20.0 ng/L of TCP were 98% and 10%, respectively.
- 12.2.4. The mean recovery and relative standard deviation for LFB samples (n=10) containing 20.0 ng/L of TCP were 94% and 11%, respectively.

12.3. Fifteen groundwater samples that were analyzed on both the GC/MS-quadrupole and the GC/MS- ion trap systems were found to contain TCP at concentrations ranging from 8 to 300 ng/L. Linear regression analysis of the measurement results from the GC/MS-quadrupole system compared with those from the GC/MS- ion trap system resulted in a slope, intercept and correlation (r^2) of 0.985, 2.39 and 0.9981, respectively.

13. References

13.1. U. S. EPA. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III (Methods504.1, 524.2 and 551.1)*; EPA/600/R-95/131; U.S. Environmental Protection Agency, Office of Research and Development: Washington, DC, August 1995.

14. Acknowledgements

14.1. The GC/MS-ion trap method was developed by J. Remoy, J. Dhoot, H. S. Okamoto and S. K. Perera, CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch-North. The GC/MS-quadrupole method was developed by P. Hill and W. R. Steeber, CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch-South.

Table 1. Instruments and Parameter Settings Employed in the Development of this Method.

BLANK	System 1	System 2
Purge and Trap Concentrator	**Tekmar 3000 with Dry Purge and Sample Heater Jacket**	**Tekmar 3000 with Dry Purge and Sample Heater Jacket**
Sample volume	25 mL	25 mL
1,2,3-Trichloropropane-D_5 (internal standard) spike concentration in sample	400 ng/L	40 ng/L
Purge: Vessel type Time & temperature Gas flow rate Dry purge time	 25 mL fritted glass sparger? 11 min. at 40°C 40 cc/min. 2 min.	 25 mL fritted glass sparger 11 min. at 40°C 40 cc/min. 5 min.
Trap: Desorb preheat temperature Desorb time & temperature Gas flow rate Bake out time & temperature	 245°C 4 min. at 250°C 20 cc/min. 8 min. at 270°C	 245 °C 4 min. at 250 °C 30 cc/min. 10 min. at 260 °C
Gas Chromatograph	**Agilent 6890**	**Varian CP-3800**
Injector: Split interface Temperature	 20:1 200 °C	 20:1 200 °C
Column	30 m x 0.25 mm DB-5.625, 1.0 µm film thickness	60 m x 0.25 mm DB-VRX, 1.4 µm film thickness
He carrier gas flow rate	0.90 cc/min.	1.5 cc/min.
Column oven temperature program	Hold 35°C for 5 min., ramp at 4.0 °C/min. to 105°C, ramp at 30 °C/min. to 170°C.	Hold 45°C for 10 min., ramp at 12 °C/min. to 190°C, ramp at 6°C/min. to 225 °C.

Retention Time: 1,2,3-Trichloropropane-D_5 1,2,3-Trichloropropane	 ~20.36 min. ~20.58 min.	 ~20.86 ~20.95
Mass Spectrometer	**Agilent 5973 MSD**	**Varian Saturn 2000 Ion Trap**
Ionization mode	EI, 70 eV, auto-tune	EI, 70 eV, auto-gain control
Filament & electron multiplier: Delay time (off) Start/end times (on) Emission current EM voltage	 19 min. 19.0/22.0 min 34.6 µA Set +300 V higher than for normal full scan mode.	 19 min. 19.0/22.0 min. 100 µA Add +200 V to auto-gain setting, +200 V added by SIS mode.
Additional ion trap parameters: Waveform amplitude SIS amplitude adjustment factor Pre-ionization time	Not applicable Not applicable Not applicable	 25 V 200 1500 µS
Scan mode	Selected ion monitoring Mass 1: 75 Mass 2: 79 Mass 3: 110	Selected ion storage Mass range 1: 74 to 82 Mass range 2: 96 to 104 Mass range 3: 109 to 116