DETERMINATION OF 1,2,3-TRICHLOROPROPANE IN DRINKING WATER BY CONTINUOUS LIQUID-LIQUID EXTRACTION AND 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. While the ion trap mass spectrometer (MS) detector was used in the development of this method, the quadrupole MS detector may also be used. To achieve the sensitivity necessary for this method, the ion trap MS must be operated in the selected ion storage (SIS) mode, while the quadrupole MS must be operated in the selected ion monitoring (SIM) mode.

1.4. The applicable ma trices 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 be familiar with USEPA method 525.2.

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. A 1 L sample is extracted for approximately 16 hours (overnight) with methylene chloride using a continuous liquid- liquid extractor. After extraction the methylene chloride extract is isolated, dried, then concentrated to 1 mL and analyzed by GC/MS. TCP is identified by matching the retention time and mass 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 to the samples and standards, such that the final concentrations in the sample extracts and standards are the same.

3. Interferences

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

3.2. Organic compounds which coelute or nearly coelute with TCP or TCP-D_5 and which yield the same fragment ions as TCP or TCP-D_5 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.

4. Safety

4.1. The toxicity or carcinogenicity of chemicals used in this method has not been fully defined. When working with these chemicals, use appropriate protection to eliminate or minimize exposure to these chemicals. Observe and employ other safety precautions described in the material safety data sheets for these chemicals. When operating analytical instruments, observe the manufacturers safety precautions and safe operating procedures.

5. Equipment and Supplies

5.1. Continuous liquid- liquid extractor, one step, for heavier than water solvents, with all glass or PTFE connecting joints, 1 L sample capacity (Corning Pyrex, Accelerated One-Step Modular, or equivalent).
  5.1.1. Recirculating hot water bath, or equivalent, for methylene chloride distillation.
  5.1.2. Recirculating chiller, or equivalent, for the cond enser.
5.2. Nitrogen evaporator for solvent evaporation (Organomation, or equivalent)
5.3. Gas chromatograph: Same as described in method 525.2.
  5.3.1. 30 meter x 0.25 mm DB-5ms with a 0.25 µm film thickness (J&W Scientific).
  5.3.2. An alternate column may be used if it provides the required separation and performance for this method.
5.4. Mass spectrometer and data system: Same as described in method 525.2, except the mass spectrometer and data system must be capable of the following.
  5.4.1. Ion trap mass spectrometer: Must be capable ofoperating in the selected ion storage mode (SIS).
  5.4.2. Quadrupole mass spectrometer: Must be capable of operating in the selected ion mode (SIM).
5.5. Sample containers: 1 L amber glass bottles with PTFE-lined screw-caps. The bottles may be purchased as pre-cleaned, level 2.
5.6. Assorted glass micro-syringes for preparing standards and fortification solutions.
5.7. Assorted volumetric flasks and vials with PTFE- lined screw-caps for the preparation and storage of standards and sample.

6. Reagents and Standards

6.1. Reagent water: free from TCP and other interfering contaminants.
6.2. Methylene chloride, capillary GC/trace analysis grade (Burdick & Jackson, or equivalent).
6.3. Methanol, pesticide grade.
6.4. Sodium sulfate, anhydrous, reagent grade. Heat at 400°C in a muffle furnace for 2 ho urs before use.
6.5. Primary standard: 1,2,3-Trichloropropane, 200 µg/mL in methanol (Ultra Scientific, or equivalent). Prepare a primary dilution standard in methylene chloride. Use the primary dilution standard to prepare the calibration standards in methylene chloride at the concentrations of 5.0, 10, 25, 50, 100 µg/L, or higher, as required.
6.6. QC solution: 1,2,3-Trichloropropane, 100 µg/mL in methanol (Chem Service, or equivalent). Prepare a 1.0 µg/mL primary dilution standard in methanol. Prepare the QC sample by adding 50 µL of the primary dilution standard to 1 L of reagent water to

produce a TCP concentration of 50 ng/L.

6.7. 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 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 amount of TCP-D_5 added should not exceed 50 ng/L in the aqueous samples and 50 µg/L in the working standards.

7. Sample Collection, Preservation and Storage

7.1. Collect samples in 1 L amber glass bottles as described in method 525.2.

7.2. If the samples contain residual chlorine, add 50 mg of sodium sulfite to the bottle 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 extracted within 14 days of collection. Analyze the concentrated extracts within 24 hours.

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 20 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 20 samples, or less. Prepare the LFB with a TCP concentration of

5.0 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.

8.2.4. Analyze at least one sample in duplicate per batch of 20 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 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 analyzed. 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.

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

9.5.3. The absolute area of the quantitation ion of the TCP-D_5 in the 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 instrument and instrument parameter settings that were used in the development of this method.

10.2. Ensure that the extractor is clean and free from contamination before proceeding with sample extraction.

10.3. Add the appropriate volume of methylene chloride (100 mL for the extractor described in Section 5.1) to the extractor's distillation flask, assemble the extractor and extract for approximately 16 hours (overnight).

10.4. To a 1 L aliquot of the sample, add an appropriate aliquot of the TCP-D_5 primary dilution solution and transfer the sample to the extractor.

10.5. After the extraction is completed, dry the methylene chloride extract with anhydrous sodium sulfate and concentrate the extract to 1.0 mL.

10.6. Analyze the sample extract using the instrument parameter guidelines in Table 1.

10.7. 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.

10.7.1. 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.

10.7.2. 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.

10.8. 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.

10.8.1. 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.

10.8.2. 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 coeluter will result in a calculated TCP spike recovery that will be lower than normal).

10.9. 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 $A_{TCP\ -D5}$ 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.
$A_{TCP\ -D5}$ = integrated abundance of the m/z 79 quantitation ion for the internal Standard, TCP-D_5.
$Q_{TCP\ -D5}$ = 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 curve established in Section 9.

12. Method Performance

12.1. Using reagent water fortified with 5.0 ng/L of TCP (n = 8), a single laboratory, single operator MDL of 0.8 ng/L was achieved for TCP. The mean recovery and relative standard deviation were 111% and 4.8%, respectively. The MDL study was conducted over a period of four days.

12.2. The mean recovery and relative standard deviation for a 50.0 ng/L TCP QC sample (n=9) were 103% and 5.0%, respectively.

12.3. The single laboratory, single operator mean recovery and relative standard deviation for 100 ng/L of TCP-D_5 in reagent water (n=22) were 94% and 15%, respectively.

12.4. The estimated reporting limit for TCP was 5.0 ng/L.

12.5. Six groundwater samples that were analyzed by this extraction method and by the purge and trap GC/MS (ion trap) method were found to contain TCP at concentrations ranging from 8 to 77 ng/L. Linear regression analysis of the results from the purge and trap GC/MS method compared with those obtained from this method resulted in a slope, intercept and correlation (r^2) of 0.932, –0.16 and 0.9914, respectively.

13. References

13.1. U. S. EPA. *Methods for the Determination of Organic Compounds in Drinking Water, Supplement III (Methods504.1, 524.2, 525.2 and 551.1)*; EPA/600/R-95/131; U.S. Environmental Protection Agency, Office of Research and Development: Washington, DC, August 1995.

13.2. "Determination of 1,2,3-Trichloropropane in Drinking Water by Purge and Trap Gas Chromatography/Mass Spectrometry," CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch, Berkeley, CA, February 2002.

14. Acknowledgements

14.1. This method was developed by J. Dhoot, H. Okamoto and S. K. Perera, CA Department of Health Services, Division of Drinking Water and Environmental Management, Sanitation and Radiation Laboratories Branch-North.

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

Gas Chromatograph and Autosampler	**Varian Star 3400 CX with 8200 CX AS**	**BLANK**
Injector: Mode Temperature Sample injection volume	Splitless for 0.7 min. 225 ^{o}C 2.0 µL	Blank
Column	30 m x 0.25 mm DB-5ms, 0.25 µm film thickness	Blank
He carrier gas flow rate	1.0 cc/min. (electronic pressure controlled)	Blank
Column oven temperature program	Hold 40 ^{o}C for 4 min., ramp at 10 ^{o}C/min. to 250 ^{o}C, hold for 5 min. at 250 ^{o}C.	Blank
MS transfer line temperature	175 ^{o}C	Blank
Retention Time: 1,2,3-Trichloropropane-D_5 1,2,3-Trichloropropane	~7.73 min. ~7.83 min.	Blank
Mass Spectrometer	**Varian Saturn 2000 Ion Trap**	**Agilent 5973 Mass Selective Detector ***
Ionization mode	EI, 70 eV, auto-gain control	EI, 70 eV, auto-tune
Filament & electron multiplier: Delay time (off) Start/end times (on) Emission current EM voltage	7.0 min. 7.0/8.5 min. 100 µA Add +200 V to auto-gain setting, +200 V added by SIS mode.	7.0 min. 7.0/8.5 min. 34.6 µA Set +300 V higher than for normal full scan mode.
Additional ion trap parameters: Waveform amplitude SIS amplitude adjustment factor Pre-ionization time	25 V 200 1500 µS	Not applicable Not applicable Not applicable

Scan mode	Selected ion storage Mass range 1: 74 to 82 Mass range 2: 96 to 104 Mass range 3: 109 to 116	Selected ion monitoring Mass 1: 75 Mass 2: 79 Mass 3: 110

*Note: Parameters taken from Reference 13.2.