



Lowering detection limits for 1,2,3-trichloropropane in water using solid phase extraction coupled to purge and trap sample introduction in an isotope dilution GC-MS method



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HIGHLIGHTS

- Combining SPE with PTI significantly reduces detection limits for 1,2,3-trichloropropane in water.
- Tandem SPE-PTI achieves a 500 mL (equivalent) sample introduction using conventional drinking water laboratory instruments.
- The method may be applicable to other carcinogenic VOCs for which there is also interest to lower detection limits.

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ABSTRACT

Purge and trap sample introduction (PTI) has been the premier sampling and preconcentration technique for gas chromatographic determination of volatile organic compounds (VOCs) in drinking water for almost 50 years. PTI affords sub parts-per-billion (ppb) detection limits for purgeable VOCs including fixed gases and higher boiling hydrocarbons and halocarbons. In this study the coupling of solid phase extraction (SPE) to PTI was investigated as a means to substantially increase enrichment and lower detection limits for the emerging contaminant, 1,2,3-trichloropropane (TCP). Water samples (500 mL) were dechlorinated, preserved with a biocide, and spiked with the isotope labeled internal standard, *d*₅-TCP. The entire 500 mL sample was extracted with activated carbon or carbon molecular sieve SPE cartridges, and then eluted with dichloromethane – excess solvent was removed in a nitrogen evaporator and diethylene glycol “keeper” remaining was dispersed in 5 mL of water for PTI GC-MS analysis. The experimental Method Detection Limit (MDL) for TCP was 0.11 ng/L (ppt) and accuracy was 95–103% in sub-ppt determinations. Groundwater samples including impaired California sources and treated water (*n* = 21) were analyzed with results ranging from below the method reporting limit (0.30 ng/L) to > 250 ng/L. Coupling of SPE with PTI may provide similar reductions in detection limits for other VOCs with appropriate physical-chemical properties.

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1. Introduction

1,2,3-Trichloropropane (TCP) is a groundwater contaminant in the U.S. and other industrialized countries. TCP is exclusively man-made and has been used as an industrial solvent, a cleaning/degreasing agent and paint remover, and a synthetic intermediate, for example, a crosslinking agent in polymer production (WHO,

2003). About 80% of TCP produced originates from epichlorohydrin manufacture. TCP also is an impurity in soil fumigants including dichloropropane/dichloropropene mixtures (DD; telone), some of which have been used extensively in California.

Due to its physical-chemical properties TCP is unlikely to sorb to soil and leaches readily into groundwater. TCP also is persistent in natural waters with a hydrolysis half-life of 44 years at pHs between 5 and 9 (ATSDR, 1992). Regulatory monitoring in California has identified TCP contamination in 372 active and standby drinking water sources (SWRCB, 2015), principally in Kern, Fresno, Los Angeles and Merced Counties. TCP is considered a contaminant of emerging concern due to mounting evidence of carcinogenicity

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in experimental animals (IARC, 1995; ATSDR, 2011) and anticipated carcinogenicity in humans (NTP, 2014).

TCP is a purgeable VOC which can be determined by purge and trap (PTI) gas chromatography (GC) and PTI gas chromatography-mass spectrometry (GC-MS) using methods such as USEPA 502.2 and USEPA 524.2, respectively – both of which are approved for drinking water compliance monitoring of regulated VOC. While TCP is not regulated by the federal government in the U. S. *per se*, California established a drinking water notification level (NL) of 5 ng/L (ppt) for TCP in 1999. In 2002, our laboratory described two analytical methods capable of achieving the state's required compliance monitoring reporting limit, also 5 ng/L (CDPH, 2002a; 2002b). More recently a revised public health goal (PHG) of 0.7 ng/L was established for TCP (OEHHA, 2009).

This paper describes further research on trace determination of TCP in finished drinking water and drinking water sources. Specifically, we investigated reducing detection limits by coupling SPE with PTI, a novel approach to substantially increase VOC enrichment and preconcentration. Preliminary experiments examined feasibility, and further experiments established the basic operating conditions for determination of TCP using conventional water laboratory instrumentation. Isotope dilution quantitation using the internal standard, d_5 -TCP, provided optimal precision and accuracy. Finally, method performance was evaluated by analyzing California groundwater samples from sites with historic TCP contamination.

2. Materials & methods

2.1. Chemicals/supplies

All solvents were obtained from Fisher Scientific (Pittsburgh, PA, USA) and were glass distilled and suitable for GC or HPLC applications. A Millipore Milli-Q-Plus water purification system (Billerica, MA, USA) supplied laboratory reagent water for all experiments. Analytical standards of TCP (5000 $\mu\text{g}/\text{mL}$ in methanol) and Supelco Supelclean ENVI-Carb Plus cartridges (400 mg, P/N 54812-U) were obtained from Supelco (Bellefonte, PA, USA). The deuterium-labeled internal standard (IS), d_5 -TCP, was obtained from Cambridge Isotope Laboratories (Tewksbury, MA, USA). Waters AC-2 Sep-Pak cartridges (400 mg, P/N JJAN20229) were obtained from Waters (Milford, MA, USA).

2.2. Instruments

An Agilent 5973 MSD mass spectrometer interfaced to an Agilent 6890 gas chromatograph (Agilent Instruments, Wilmington, DE, USA) was used. The GC-MS was equipped with a Tekmar 3000 automated purge and trap sampler (Teledyne Tekmar, Mason, OH, USA). The mass spectrometer was operated in electron ionization (EI) mode with an ionization energy of 70 eV. The instrument was autotuned and electron multiplier (EM) voltage was increased by 300 V to increase signal. In addition, selected ion monitoring (SIM) was used to lower detection limits. Two ions were monitored: $\text{C}_3\text{H}_4\text{Cl}^+$ (m/z 75, 10 ms dwell time) and $\text{C}_3\text{D}_4\text{Cl}^+$ (m/z 79, 5 ms dwell time). A J & W DB-5.625 column (30 m \times 0.25 mm, 1 μm) (J & W Scientific, Folsom, CA, USA) was used with the following GC operating conditions: split interface split ratio/temp. (20:1/200 $^\circ\text{C}$); helium carrier gas (0.90 mL min^{-1}); oven temp. program (35 $^\circ\text{C}$, 5 min; 4 $^\circ\text{C min}^{-1}$ to 100 $^\circ\text{C}$; 30 $^\circ\text{C min}^{-1}$ to 170 $^\circ\text{C}$); and transfer line (220 $^\circ\text{C}$). The purge and trap sampler operating conditions were: sample volume (5 mL); purge vessel (25 mL fritted sparger); purge time/temp./He flow rate (11 min/40 $^\circ\text{C}$ /20 mL min^{-1}); dry purge (2 min). A Tenax trap was used: desorb preheat (245 $^\circ\text{C}$); desorb (4 min at 250 $^\circ\text{C}$); desorb gas (20 mL min^{-1} He); bake out (8 min at 270 $^\circ\text{C}$). The retention times were: d_5 -TCP (20.35 min) and

TCP (20.56 min) and a filament delay of 19 min was used.

2.3. Analytical procedure

After preliminary experiments to identify the optimal sample preparation conditions, the following procedure was adopted. Samples were extracted manually using ENVI-Carb Plus SPE cartridges mounted on an extraction manifold. The SPE cartridges were conditioned by washing with 3 mL of dichloromethane, 2 mL of methanol, and a second aliquot of 2 mL of methanol followed by 2 mL of laboratory reagent water. The sorbent was not allowed to run dry during conditioning. Water samples (500 mL) were fortified with 10 ng/L of the IS, d_5 -TCP, by transferring 10 μL of a 500 ng/mL methanolic solution. Water samples were then loaded onto the cartridge with a flow rate of ~ 10 mL/min. The receiver was removed and air was drawn through the cartridge for 2 min. To elute retained analytes, the cartridges were inverted, the cartridge reservoir was filled with methylene chloride, and the sorbent was soaked in the solvent for ~ 1 min without vacuum. Methylene chloride was then eluted dropwise under a low vacuum. Methylene chloride was dried by percolation through 0.4 g of anhydrous sodium sulfate in a small column and the extract was combined with 50 μL of diethylene glycol-methylene chloride (1:1, v/v). The sample was concentrated under a gentle stream of nitrogen in a room temperature water bath to a final volume of 50–75 μL prior to addition of 5 mL of laboratory reagent water. The sample was vortexed to disperse the solvent “keeper” thoroughly prior to transfer of the sample to the purge vessel.

3. Results

3.1. Performance of existing methods

A number of instrumental methods have been used to determine TCP in drinking water including PTI GC (e.g., USEPA 502.2 with electron capture detector (ECD)) and PTI GC-MS (e.g., USEPA 524.2 and USEPA 524.3). In addition, enrichment and preconcentration of TCP has been accomplished by solvent extraction with either hexane (USEPA 504.1 with ECD-GC analysis) or MTBE (USEPA 551.1). MDLs for TCP vary considerably among these procedures (Table 1). The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined by analysis of samples in a given matrix containing the analyte (CFR, 1984). MDLs vary according to many factors both within and between laboratories (Draper et al., 1998). Because reliable quantitation is possible only at concentrations above the MDL, method reporting limits are ideally 3- to 5- times the MDL. Accordingly, an MDL of 1.7 ng/L has been required to achieve the current, mandatory TCP reporting limit of 5 ng/L.

Since 2002, CDPH has recommended modified or alternative methods (CDPH, 2002a; 2002b) with increased detection capability for TCP regulatory monitoring. USEPA Method 524.2, for example, was modified by use of SIM in quadrupole instruments and selected ion storage (SIS) in quadrupole ion trap instruments increasing sensitivity relative to mass scanning. Other modifications such as the 25 mL sample volume and detector adjustments further boosted sensitivity. Yoo et al., (2005) lowered reporting limits for TCP (and 1,4-dioxane) by improving purge efficiency 2-fold with a 20 min purge time, and by use of MS-MS with a 50-fold increase in detector response. Similar approaches have been used in other monitoring programs. Miermans et al. (2000) determined TCP with an MDL of 0.4 ng/L using PTI with a quadrupole ion trap instrument and a modified sample introduction device, a condenser followed by liquid nitrogen-cooled, fused silica trap.

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