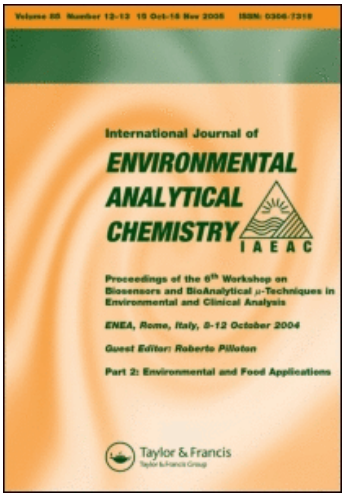

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A Validated GC-MS Assay for the Quantitation of Trichloroethylene (TCE) from Drinking Water

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A VALIDATED GC-MS ASSAY FOR THE QUANTITATION OF TRICHLOROETHYLENE (TCE) FROM DRINKING WATER

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Trichloroethylene (TCE) is a common ground and surface water contaminant found in the United States. A validated GC-MS assay for the quantitation of TCE in drinking water is presented here. The limit of quantitation, 5 μg/L, is lower than current validated methods for the analysis of TCE from water. This assay requires a small sample volume, has simple sample preparation, fast run time, high recovery, and reproducible and accurate results.

Keywords: Trichloroethylene; TCE; GC-MS; Liquid–liquid extraction; Drinking water

INTRODUCTION

Trichloroethylene (TCE) is a common industrial solvent that has been used for over 100 years as a metal degreaser, anesthetic, chemical intermediate, and dry cleaning agent [1,2]. The presence of TCE in the environment can be attributed to industrial discharge of the chemical to and leaching from hazardous waste sites [1]. As a result of its widespread and long-term use, TCE can be found in groundwater at more than 50% of the hazardous waste sites on the United States Environmental Protection Agency's (EPA's) National Priorities List [1]. A 1989 survey indicated that TCE could be found in more then 34% of municipal drinking water supplies in the United States [3]. Concentrations found in U.S. water supplies vary from levels below the EPA's acceptable limit (5 ppb) to levels up to 239 and 267 ppb in contaminated sites of Tucson, AZ and Woburn, MA respectively [1,4,5]. TCE is also one of the chemicals found to be prevalent in blood samples from the general population, detectable in 10% of the samples taken in the Third National Health and Nutrition Examination

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(NHANES III) conducted by the U.S. Centers for Disease Control [6]. Exposure to TCE has been linked to central nervous system (CNS) depression, cardiac arrhythmias, and some cancers [1,7,8].

The U.S. EPA currently uses a GC-ECD method for the analysis of TCE from drinking water (EPA Method 551.1) [9]. This method requires a liquid–liquid extraction with methyl-tert-butyl ether (MTBE) or pentane, as an alternative solvent; however, the EPA recognizes the potential for these solvents to be contaminated with TCE. As a result, multiple distillations of the MTBE or pentane may be required prior to analysis, thus delaying analysis of highly volatile samples. Other groups report very low limits of quantitation for TCE from water, but provide no information on assay validation [10,11]. Large sample sizes (up to one liter) are also required by some methods to attain reported limits of detection [11]. We report here a new method using diethyl ether extraction and GC-MS detection using selected ion monitoring (SIM) that offers improved quantitation of TCE from drinking water.

EXPERIMENTAL

Materials

Analytical grade TCE was purchased from Aldrich (Milwaukee, WI, USA). Anhydrous diethyl ether was purchased from J.T. Baker (Phillipsburg, NJ, USA). Perfluorokerosene was obtained from Sigma (St. Louis, MO, USA). The deionized water was generated from a Continental Deionized Water System (Natick, MA, USA).

Instrumentation

A Hewlett Packard (Agilent) 5890 Series II gas chromatograph (Palo Alto, CA, USA) interfaced with a Micromass AutoSpec magnetic sector mass spectrometer with an electron ionization source (Manchester, UK) was used for all GC-MS experiments. The resolution of the mass spectrometer was kept at 1500 and the electron energy at 70 eV. The source temperature was 100°C and the GC transfer line was maintained at 200°C. A LEAP Technologies CTC-A200S Autosampler (Carrboro, NC, USA) with an SGE gas-tight syringe (Victoria, Australia) was used for sample introduction. A DB-5ms capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) from J & W Scientific/Agilent (Palo Alto, CA, USA) was used for all chromatographic separations. The GC temperature program was isothermal for 4 min at 35°C with TCE eluting at ~3.5 min. The helium flow rate was 30 cm/min. The injector was operated in the splitless mode and kept at 100°C. Each sample injection volume was 2 μL.

Procedure

A stock solution of 10 mg/L TCE was prepared in deionized water. From the stock solution, dilutions of 1 mg/L, 600, 400, 200, 100, 60, 40, 20, 10, 5, and 1 μg/L were made in deionized water. Dilutions of 750, 75, and 7.5 μL were also made for use in the assessment of assay precision and accuracy. A new set of stock and standard solutions were made on each day of validation.

Samples were prepared by adding 200 μL diethyl ether to 200 μL of water sample into a conical bottomed glass vial. Samples were capped and vortexed for 15 s using a Scientific Industries Vortex Genie 2 (Bohemia, NY, USA). Once phase separation had occurred, the ether layer was transferred to an autosampler vial and analyzed.

The mass spectrometer was calibrated daily using perfluorokerosene (PFK). The SIM voltage experiment was used in the quantitation of TCE. The PFK peak of m/z 130.99202 was used as a lock mass for the monitoring of the TCE molecular ion, m/z 129.9144.

The assay was validated over three different days. A ten-point calibration curve was generated on each day with the following calibration points: 1 mg/L, 600, 400, 200, 100, 60, 40, 20, 10, and 5 μg/L. Blanks of the deionized water and a 1 μg/L limit of detection (LOD) sample was run on each day of validation. The LOD was determined by a 3 : 1 signal to noise ratio. Five replicate samples of 750, 75, and 7.5 μg/L were prepared each day to test precision and accuracy. Each calibration and validation sample was injected in duplicate. Precision was expressed in terms of relative standard deviation: % RSD = 100* (SD/mean). Accuracy (% Error) was expressed as the percent difference between the theoretical concentrations and the experimental concentrations of the replicate samples in each validation set. Microsoft Excel was used to generate linear regression equations for the calibration curves and to calculate the RSD and the error for each validation set.

RESULTS AND DISCUSSION

Sample chromatograms for a blank water extract and a water extract at the limit of quantitation (5 μg/L TCE) are shown in Fig. 1. The absence of interfering matrix peaks is attributed to the use of the SIM voltage experiment for monitoring TCE. An external calibration technique is used because addition of a second analyte to the experiment would lower the sensitivity of the assay. The possibility of using deuterated (d^1) TCE was investigated, but the increase in resolution required to resolve d^1-TCE from the PFK calibrant peak at m/z 130.99202 would have drastically lowered the sensitivity.

Several chemicals were tested for possible liquid–liquid extraction solvents including, MTBE, pentane, chloroform, *n*-hexane, toluene, isooctane, ethyl acetate, and petroleum ether. The highest recoveries of TCE were obtained with MTBE, pentane and diethyl ether extraction; however, MTBE and pentane were not ultimately chosen for the extraction solvent because of the high frequency of TCE contamination of different solvent batches. Many other commercially available solvents also had the consistent problem of high TCE background levels. In some cases, diethyl ether batches contained trace quantities of TCE, but due to the wide range between diethyl ether and TCE boiling points, the TCE could be removed with a single simple distillation.

Because the calibration standards were made in deionized water and real samples were measured in tap water it is important to determine if there are any matrix effects. The use of selected ion monitoring and moderate resolution in the mass spectrometer make it unlikely that there would be any interference. However, samples at a concentration of 100 μg/L ($n = 5$) prepared in each matrix were compared. The samples were found to be statistically indistinguishable ($p = 0.05$).

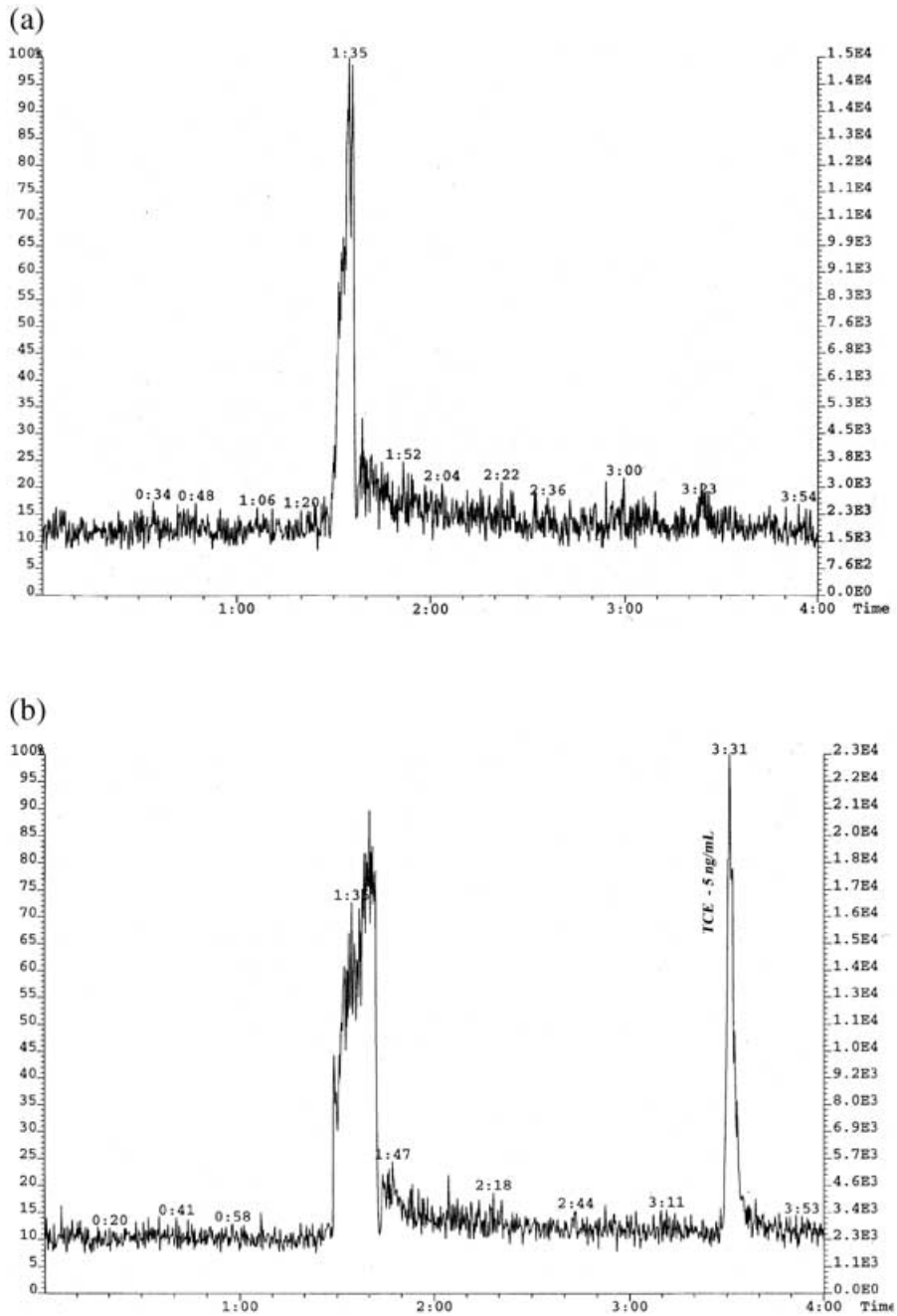

FIGURE 1 Blank water extract (a) and spiked water extract at the 5 μg/L level (b).

Over the three days of validation, the assay demonstrated a RSD and an error $< 15\%$. This data is shown in Table I. Recovery was evaluated at the 100 μg/L level by comparing 5 water extracts with ether standards of the same concentration. The recovery for the assay was $96.9 \pm 3\%$. The method was linear over the tested

TABLE I The precision (% RSD) and accuracy (% Error) of TCE quantitation from water over 3 days ($n = 30$ for each validation concentration)

Concentration TCE added (μg/L)	*Concentration TCE found* (μg/L) *average* ± *SD*	*% RSD*	*% Error*
7.5	7.92 ± 0.59	7.46	7.73
75	72.8 ± 7.8	10.7	8.52
750	648.2 ± 81.1	12.5	14.7

TABLE II Comparison of the analytical figures of merit of EPA Method 551.1 to the current method

Parameter	*EPA*	*UGA*
Sample size	10 mL	200 μL
Volume extraction solvent used	3 mL (MTBE)	200 μL (diethyl ether)
Recovery	94 ± 6%	97 ± 3%
Instrumental method	GC-ECD	GC-MS
RSD range	1.20–8.68%	7.46–12.5%
Method detection limit	0.04 pg	0.4 pg
R^2	Not reported	0.9902
Retention time (TCE)	12.61 min (DB-1)	3.5 min (DB-5)

range with an average r^2 value for the calibration curves of 0.9902. The method detection limit was determined to be 0.4 pg of TCE on column. A comparison of the analytical figures of merit between this method and the US EPA method 551.1 is shown in Table II [9]. The strength of the current method is that it is faster and requires a lower sample volume then the current EPA method, while maintaining comparable precision and recovery. The EPA method is an order of magnitude more sensitive; however, both methods can determine samples below the current regulatory limit.

CONCLUSIONS

This assay is a fast, simple, and reproducible way to measure a wide range of TCE concentrations in drinking water. The recovery for diethyl ether liquid–liquid extraction is high and the use of this solvent minimizes the concern for TCE contamination. The method was linear having an average r^2 value of 0.9902 and an on-column method detection limit of 0.4 pg. Unlike other methods for measuring TCE from water, this assay has been validated over three days demonstrating a RSD $< 13\%$ and an error $< 15\%$.

Acknowledgements

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