Simultaneous Determination of Chlorinated Ethenes and Ethene in Groundwater Using Headspace Solid-Phase Microextraction with Gas Chromatography

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Received 20 April 2012; revised 10 December 2012

Widespread contamination of groundwater by chlorinated ethenes and their biological dechlorination products necessitates the reliable monitoring of liquid matrices; current methods approved by the U.S. Environmental Protection Agency (EPA) require a minimum of 5 mL of sample volume and cannot simultaneously detect all transformative products. This paper reports on the simultaneous detection of six chlorinated ethenes and ethene itself, using a liquid sample volume of 1 mL by concentrating the compounds onto an 85-μm carboxen-polydimethylsiloxane solid-phase microextraction fiber in 5 min and subsequent chromatographic analysis in 9.15 min. Linear increases in signal response were obtained over three orders of magnitude (∼0.05 to ∼50 μM) for simultaneous analysis with coefficient of determination (R²) values of ≥0.99. The detection limits of the method (1.3–6 μg/L) were at or below the maximum contaminant levels specified by the EPA. Matrix spike studies with groundwater and mineral medium showed recovery rates between 79–108%. The utility of the method was demonstrated in lab-scale sediment flow-through columns assessing the bioremediation potential of chlorinated ethene-contaminated groundwater. Owing to its low sample volume requirements, good sensitivity and broad target analyte range, the method is suitable for routine compliance monitoring and is particularly attractive for interpreting the bench-scale feasibility studies that are commonly performed during the remedial design stage of groundwater cleanup projects.

Introduction

The chlorinated ethenes perchloroethylene (PCE) and trichloroethylene (TCE), once widely used in industry as metal degreas- ing agents and as solvents in dry cleaning, are classified as probable and known human carcinogens, respectively (1). These compounds are widespread contaminants of groundwater, as are their various products of chemical, biological and physical transformation, including the three isomers of dichloroethylene (cis,1,2-, trans,1,2- and 1,1-DCE), and vinyl chloride (VC), a known human carcinogen (2). Anaerobic reductive dechlorination of these chlorinated ethenes involves the stepwise replacement of each chlorine atom with a hydrogen atom to the end product ethene.

To conduct a mass balance to monitor the desirable anaerobic, reductive process of microbiological dechlorination of these compounds, it is critical to have a method capable of simultaneous detection of the parental chlorinated ethenes, their lower chlorinated intermediates and the non-chlorinated end product, ethene. The U.S. Environmental Protection Agency (EPA) maximum contaminant levels (MCLs) for these compounds are all in the low μg/L range. To obtain sufficiently low method detection limits (MDLs) with headspace injection, the minimum liquid volume using U.S. EPA Method 5021A is 10 mL. U.S. EPA Method 624 involves the sample concentration approach called purge and trap, reducing the liquid volume requirement to 5 mL (3). Whereas this volume is only a fraction of the volume of a standard U.S. EPA volatile organic analysis (VOA) 40 mL vial, it still represents a challenge in commonly performed remediation feasibility studies that require the repeated sampling and analysis of laboratory-scale reactors and microcosms (4–8). This analytical challenge is common to the long established groundwater remediation industry and to the emerging field of bioenergy production using contaminated process water.

Various studies describe the use of solid-phase microextraction as a means for concentrating analytes from sample head-space (HS-SPME) followed by gas chromatography (GC) flanked by detection using either a flame ionization detector (FID), electron capture detector, (ECD) or mass spectrometry (MS) for the analysis of PCE, TCE, DCE or a combination of these (9–12). None of these methods, however, include the analysis of VC and ethene. In addition, most of these methods use liquid volumes of 5 mL or greater and require below room temperatures for the extraction. A detailed review of HS-SPME is provided by Zhang and Pawliszyn (13), and a comparison between HS-SPME versus purge and trap is provided by Lara-Gonzalo et al. (14).

Song et al. (15), Wymore et al. (16) and Chung et al. (7) note the use of HS-SPME-GC–FID for analysis of TCE, cis-DCE, VC and ethene from groundwater samples, but none describe the method in detail. Song et al. (15) state that the analyses were conducted with a 75 μm carboxen-PDMS fiber, but a full description of the method was not published. Wymore et al. (16) validated their method by sending various samples to off-site laboratories that used U.S. EPA methods and receiving blind samples from an independent vendor to analyze on-site; they too do not further describe their method. Chung et al. (7) provide the greatest detail on their method, e.g., fiber type, adsorption time, column and temperature profile, and note that the SPME was conducted manually. Their calibration approach, however, was conducted in 160 mL serum bottles with 100 mL of liquid, whereas the samples were analyzed in 2.5 mL vials.
with 2 mL of liquid. It may be possible to scale the analyses for different liquid and HS volumes, but this would impinge on achieving the desired low detection limits. Thus, the method requires further validation.

This study describes the first HS-SPME-GC-FID method able to simultaneously detect PCE, TCE, cis-, trans-, and 1,1-DCE, VC and ethene; the method was tested in synthetic and actual groundwater. Furthermore, this method is automated and uses a sample volume of only 1 mL, which is ideal for laboratory settings. It has recently been successfully applied by Ziv-El et al. (8), who studied a lab-scale membrane biofilm reactor (MBR) whose application is reductive dechlorination of TCE in groundwater. This study also presents results in which this method was used in a feasibility study to assess bioremediation using a lab-scale sediment flow-through column.

Experimental

Sample preparation

One mL liquid samples were analyzed in 2 mL crimp top vials with a magnetic cap and silicon/polytetrafluoroethylene (PTFE) septa (MicroSOLV Eatontown, NJ). The samples were vortexed inverted for 1 min to promote rapid mass transfer of the chemicals into the vial headspace.

Analysis

The samples were processed with an AOC-5000 autosampler as follows (Shimadzu, Columbia, MD). The vials were heated and vortexed in an agitator oven at 30°C for 1 min, followed by a 5-min adsorption period by SPME, using an 85 μm carboxen-polymethylsiloxane (PDMS) fiber (Supelco, Bellefonte, PA), followed by 5 min of desorption into a gas chromatograph equipped with a flame ionization detector (Shimadzu GC-2010). The compounds were separated with an Rt-QSPLOT column of 30 m length, 0.32 mm i.d., and 10 μm film thickness (Restek, Bellefonte, PA). Helium was the carrier gas, flowing at a rate of 1.85 mL/min. To optimize the practical range of the method, a split ratio of 10 was selected, which offered a good balance between low MDLs and a broad linear range of the method, a split ratio of 10 was selected, which

Calibration curves, limits of detection and linearity

The calibrations were conducted with neat PCE (Sigma Aldrich, St. Louis, MO), TCE (Sigma Aldrich), cis-, trans-, and 1,1-DCE (Supelco), gaseous VC at 99.5% (Fluka, Milwaukee, WI) and gaseous ethene at 99.5% (Matheson Tri-gas, Basking Ridge, NJ).

For PCE, TCE, cis-DCE, trans-1,1-DCE and 1,1-DCE, a stock solution, described in Supplementary Table IA, was prepared in 245 mL serum bottles containing a Teflon-lined stirring bar and filled with deionized water, leaving no headspace, capped with a PTFE-lined stopper and crimped. The solution was stirred at room temperature for 4 h before use. A second stock solution was prepared by a two orders of magnitude dilution into the same serum bottle setup described previously. Details of the VC and ethene stock concentrations are provided in Supplementary Table IB. The concentrations were prepared in 120 mL serum bottles holding a PTFE-lined stirring bar, capped with a PTFE-lined stopper and crimped. The mixtures were stirred for 4 h before use.

Varying volumes of the liquid stock solutions were added to the 2 mL sampling vials with a gas-tight syringe containing deionized water to provide a final volume of 1 mL; the final concentrations and preparation details are in Supplementary Table IC. The gaseous stock solutions were then added as listed in Supplementary Table ID. Before adding the stock solutions of liquid and gas, the volume equivalent to that being added was removed from the vial headspace to minimize chemical losses due to over-pressurization.

The MDLs were determined as described previously (17). Seven blank samples were analyzed and the signal mean and standard deviation were determined. The MDL was the lowest concentration analyzed for which the signal for seven samples was always larger than three standard deviations above the mean of the blanks.

The limits of linearity were determined as the concentration range for which the coefficient of determination (R²) was greater than 0.99. A seven-point calibration was then conducted in triplicate.

Recoveries of Arizona groundwater and anaerobic mineral medium

The recoveries of the compounds (n = 4) were tested in Arizona groundwater and in anaerobic mineral media (18), typical of that used for anaerobic reductive dechlorination feasibility studies, with spiked samples containing target analytes at concentrations within 9–36 μM. The spiked concentration values for each in μM and mg/L are in Table I.

Maximum holding time for abiotic samples

The maximum time that samples can be stored was defined as the time for which the compound recoveries remained in the range of 90 to 110%. Triplicate samples were tested by spiking deionized water with target analytes to final concentrations of 10–30 μM and subsequent analysis after temporal storage in two conditions: upright in the autosampler at room temperature and inverted at 4°C, to minimize losses through the cap.
**Lab-scale sediment flow-through column study**

The utility of the HS-SPME-GC–FID method was assessed in a bench-scale feasibility study design typical of the groundwater remediation industry. A lab-scale sediment flow-through column, whose setup is in Figure 1A, was inoculated with the mixed-microbial consortium DehaloR² (19) and fed with groundwater containing TCE at a concentration of \( \approx 50 \mu g/L \). The influent-feed cycle was 56 \( \mu \)L for 90 s, followed by a 240 s pause, resulting in an effective feed-rate of 0.91 mL/h. Influent and effluent samples were taken periodically with a gas-tight syringe by sampling 0.2 mL and diluting in 0.8 mL of deionized water, and analyzed as described previously.

**Results and Discussion**

All seven compounds—PCE, TCE, cis-DCE, trans-DCE, 1,1-DCE, VC and ethene—could be separated and analyzed simultaneously, as shown in the chromatogram in Figure 2. The adsorption and desorption times, injector and detector temperatures, and column temperature profile were optimized with extensive screening to provide maximum signal response and to ensure no carry-over of analytes. The MDLs for all the compounds, listed in Table II, were at or below the U.S. EPA MCLs, except for VC, with which the MDL was slightly (0.5 \( \mu g/L \)) above the MCL. Pagé and Lacrois (20) demonstrated that lower detection limits can be achieved with a fiber coated with carboxen/PDMS as opposed to PDMS alone. Furthermore, analyzing TCE in municipal sewage, Wejnerowska and Gaca (21) report a four times lower detection limit using an ECD (0.005 \( \mu g/L \)) instead of an FID (6 \( \mu g/L \)), which may improve the detection limits for the method described in this study. However, such modifications are nonessential for feasibility studies (4–6) and would be beneficial mostly if the method was applied to environmental monitoring for compliance purposes. For remediation feasibility studies, replacement of the FID with a halogen-responsive ECD is counter-productive, because it makes impossible the simultaneous detection of the fully dechlorinated product ethene along with its chlorinated parental compounds. Although MS detection can add crucial information, FID is much more broadly available and less expensive to perform.

Using extensive screening, it was found that the linear range of this method extended across three orders of magnitude for all seven compounds when monitored jointly (Table II) and could be extended further for at least one order of magnitude when analytes were assayed individually. As a comparison, Poli et al. (11) reported a linear range of four orders of magnitude for PCE and TCE analysis in urine with an MS detector. Fabbri et al. (22) observed linearity across three orders of magnitude in concentration for olive oil samples. Wejnerowska and Gaca (21) achieved linearity across a single order of magnitude using an FID and twice that when using an ECD.

Analyte recoveries in Arizona groundwater and mineral medium, reported in Table I as the percent recovery compared to spiked deionized water, were minimally sensitive to the aqueous sample matrix assayed (Table I). The recoveries of PCE, TCE and the three DCE isomers were 99–108% for groundwater and 94–100% for anaerobic mineral medium; these recoveries were similar to those reported by Wu et al. (23), who analyzed industrial wastewater samples. The recoveries for VC and ethene were lower: \( \approx 90% \) in groundwater and \( \approx 80% \) in the mineral medium, respectively. Other studies have analyzed samples from a diverse group of liquids including vegetable oil (20), olive oil (24), municipal sewage (21), urine (11) and rat blood (25). No studies have reported the method development for these compounds in groundwater or mineral medium, and the studies referenced previously did not assess compound recoveries.

Furthermore, the impact of sample storage for vials kept upright at room temperature in the autosampler and inverted at 4°C (Supplementary Figure 1) was studied, and the corresponding maximum holding times were calculated (Table III). Samples were stable for up to 1 h in the autosampler and at least 47 h at 4°C. Other studies using autosamplers (7, 8, 24) do not report holding times. The use of a chilled autosampler could potentially extend the sample holding times reported here, but this equipment is not widely available in typical lab settings.

Finally, the method was applied to the analysis of a lab-scale sediment flow-through column experiment, operated in triplicate, to examine the time course of biological reductive dechlorination of TCE to ethene (Figure 1). In Figure 1B are the results for a representative column. One measurement was...
taken for each sediment column at each time point and trends were similar across the columns. The method was successful in tracking reduction of TCE to $\text{cis}$-DCE, VC and ethene over an 80-day span with starting concentrations in the low $\mu$g/L range. The sum of the products at any point (i.e., the mass balance) fluctuated by 40% at most. These fluctuations are indicative of sorption phenomena taking place in the experimental setup.

Based on the results, this method appears best suited for laboratory feasibility studies, such as small-scale sediment columns or water treatment technologies (7, 8), in which the sample volume is limited and samples are immediately processed to obtain an optimal mass balance. The method also may serve for compliance monitoring when sample volumes are limited and prevent the use of conventional EPA standard methods.

Conclusions
A rapid, simple and replicable method was developed for the simultaneous detection of chlorinated ethenes and ethene...
Samples were held upright in the autosampler or inverted at 4°C. The table below provides maximum holding times for triplicate samples in a high range of the calibration curve:

**Table III**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum holding time in autosampler (h)</th>
<th>Maximum holding time at 4°C (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCE</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>TCE</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>1,1-DCE</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>VC</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Ethene</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

*Samples were held upright in the autosampler or inverted at 4°C.

Quantification with a linear range across at least three orders of magnitude and detection at or below the EPA MCLs. This method is advantageous for the analysis of biological reductive dechlorination, in which the detection of ethene is essential to detect and monitor the desired outcome. Additionally, the small (1 mL) required sample volume and the ability of the method to simultaneously track chlorinated ethene conversion and ethene evolution make it particularly well suited for bench-scale experiments, in which the reactor volume is often small, as in the sediment flow-through columns presented here and by Ziv-El et al. (8).

References

