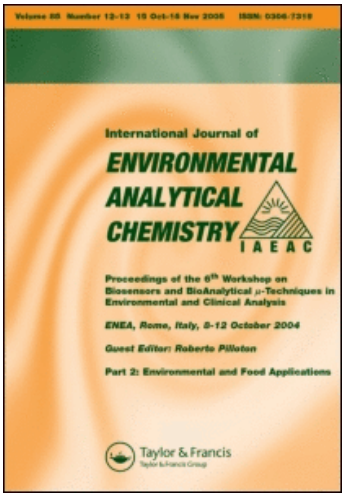

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ANALYSIS OF CHLORINATED ETHENE REDUCTION PRODUCTS IN VAPOR/WATER PHASE SYSTEMS BY DUAL-COLUMN, SINGLE-DETECTOR GAS CHROMATOGRAPHY

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A dual-column gas chromatographic method using column sequence reversal (foreflushing) for the analysis of chlorinated ethenes (e.g., tetrachloroethylene and trichloroethylene) and their common reduction products including vinyl chloride, acetylene, ethene and ethane in headspace samples is described. The chlorinated ethenes and the C_2 hydrocarbon gases are separated on 1% SP-1000 (60/80 mesh Carbopack B) and Carboxen 1000 (60/80 mesh) packed columns, respectively, and detected on a single flame ionization detector. Simulaneous determination of the chlorinated ethenes and C_2 hydrocarbon gases facilitates pathway, mass balance and kinetic studies on reductive transformations of chlorinated ethenes. The use of a single detector simplifies system calibration, data collection and interpretation. Example chromatograms using this method on three different applications are presented to illustrate its utility.

KEY WORDS: Gas chromatography, dual-column, foreflushing, chlorinated ethenes, hydrocarbon gases.

INTRODUCTION

The chlorinated ethenes, tetrachloroethylene (PCE) and trichloroethylene (TCE), have been used extensively as degreasing and dry cleaning solvents. Past disposal practices and accidental discharges have led to wide-spread contamination of subsurface environments. Some of the properties of PCE and TCE (ability to sink below the water table, low water solubilities, and relative resistance to degradation) make them susceptible to the creation of large, long-term contaminated groundwater plumes.

Natural and engineered processes capable of degrading PCE and TCE have gained considerable attention in recent years. Microbial[1,2], biochemical[3], and abiotic[4] processes are able to reduce PCE and TCE to at least one of the non-chlorinated C_2 compounds (acetylene, ethene and ethane), which are considered to be non-toxic at low concentrations. Analysis of the chlorinated ethenes, including the dichloroethylenes (cis-1,2-DCE, trans-1,2-DCE, and 1,1-DCE) and vinyl chloride (VC), and the non-chlorinated C_2 compounds is required when studying these degradation systems.

The general analytical approach has been to use one GC procecure for the chlorinated ethenes, including the dichloroethylenes (DCE) and vinyl chloride (VC), and an entirely separate second GC procedure for the non-chlorinated C_2 compounds. This approach

can be time consuming and instrument intensive. It may also be difficult to attain the precision and accuracy required for adequate mass balance determinations since multiple injections and detectors (thus, multiple calibrations) are used. DiStefano *et al.*[5] developed a single injection GC method which used two columns, two gas switching valves and three detectors to determine all the compounds of interest plus H_2. This procedure was a significant improvement in terms of time savings and the use of a single injection. The procedure is, however, instrument-intensive since multiple detectors and integrators are required.

Dual-column GC with column sequence reversal (e.g., foreflushing), single injection and a single detector is an approach that can be considered when one column separates some of the components but does not retain a second suite of sample analytes. In this procedure, the unretained components are eluted onto a second column which is able to separate those components. A valve is used to switch the sequence of the columns after the original unretained components are on the second column. The original unretained components are separated on the second column and allowed to pass unretained through the first column again and into the single common detector. The resulting chromatogram is the superimposition of two chromatographic separations. Attention is required to avoid merging of peaks from the two separations. This general approach was developed by Willis[6] for the analysis of gases. A modification of this approach was used in the analysis of hexene hydroformylation products[7].

PCE and TCE and their reduction products are well suited for analysis by the single injection and detection, column sequence reversal, dual-column GC approach. An analytical procedure for these compounds in headspace samples from vapor/water phase systems is presented. Example results of this method from three different applications are given to illustrate its utility.

MATERIALS AND METHODS

Chemicals

The chemicals used were PCE (Baker UV-Spec grade), TCE (Fisher, cert. reagent grade), cis-1,2-DCE (Aldrich), trans-1,2-DCE (Supelco), 1,1-DCE (Aldrich), n-pentane (Baxter, pesticide grade), VC (1000 ppm in N_2, Scott Specialty Gases), C_1 and C_2 hydrocarbon gases (1% each of acetylene, ethene, ethane, and methane in N_2, Scott Specialty Gases), propane (1% in N_2, Aldrich), n-butane (10% in N_2, Aldrich), titanium trichloride (13% in 20% HCl, Fluka), sodium citrate (Fisher, cert. reagent grade), vitamin B_{12} (Sigma), iron metal filings (Fisher, 40 mesh), and pyrite (Ward's Natural Science Est., Inc.). The iron was pretreated by washing in Ar-sparged 1N HCl with periodic shaking for 30 min, then rinsed thoroughly with Ar-sparged deionized water and dried at 100°C under a N_2 atmosphere. The pyrite was ground to a fine powder with mortar and pestle before use. Both the iron and pyrite were stored under an Ar atmosphere.

Gas chromatography

A Hewlett-Packard 5890 GC was configured as shown in Figure 1. Column 1 was a 1% SP-1000 on 60/80 Carbopack B column (8 ft × 1/8 in stainless steel (ss), Supleco) and column 2 was a 60/80 Carboxen 1000 column (4 ft × 1/8 in ss, Supelco). The initial

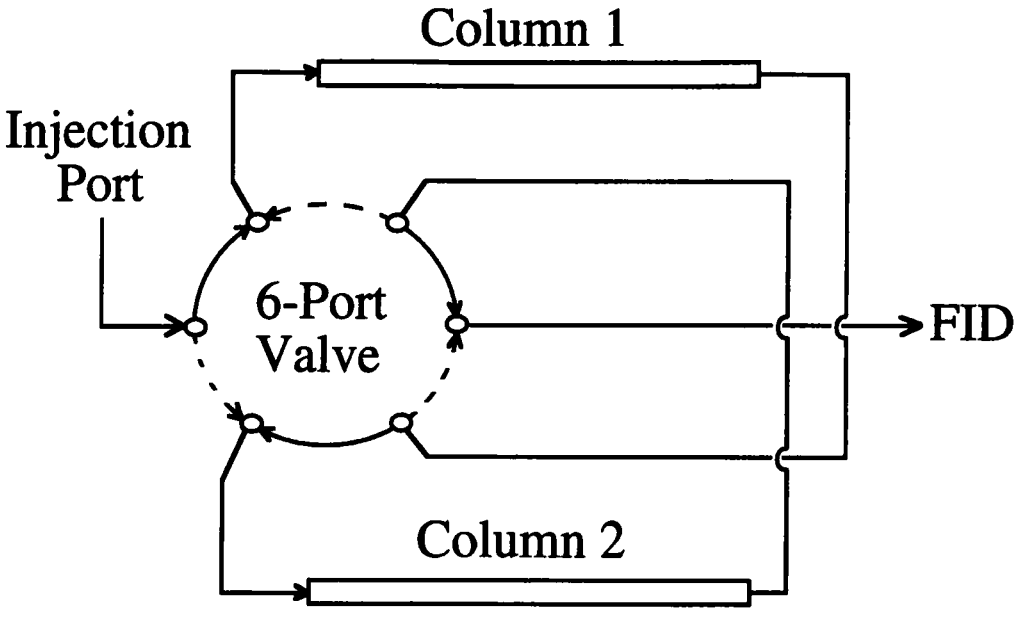

Figure 1 Schematic of dual column gas chromatography with column sequence reversal procedure for the analysis of chlorinated ethenes and reduction products. Column 1 is an 8 ft × 1/8 in ss column packed with 1% SP-1000 on 60/80 Carbopack B. Column 2 is a 4 ft × 1/8 in ss column packed with 60/80 Carboxen 1000. Solid and dashed arrows in valve indicate the valve positions before and after 1 min runtime, respectively.

column sequence was column 1 followed by column 2. The sample was injected splitless at 200°C. Carrier gas was He at 30 ml/min with inlet pressure programmed for constant flow (initial inlet pressure = 35 psi). Oven temperature program was 60°C with a 1 min hold, ramp 18°C/min to 210°C and hold for 3 min. The valve (6-port 1/8 in ss, Valco) was rotated at 1.0 min runtime. The carrier gas flow directions for both of the columns remained the same regardless of valve position. Flame ionization detector (FID) temperature was 240°C. A wide-bore FID jet was used.

Standards were prepared by adding known masses of compounds of interest to 160 cc serum vials containing 100 ml water (deionized, Milli-Q). The vials were sealed with Teflon-lined septa. n-Pentane was used as an internal standard (ISTD). Partitioning between the two phases was allowed to occur at 20°C prior to sampling the headspace for analysis. Identical vapor and water phase volumes were used in the iron and vitamin B_{12} reaction systems, so vapor:water partitioning (Henry's Law) was accounted for and concentrations could be determined as mass of compound in vapor and liquid phases within vial. Concentrations in the aqueous and vapor phases can be calculated using Henry's Law coefficients.

Anaerobic microbial consortium

A PCE-degrading anaerobic microbial consortium was provided by Dr. Jim Gossett (Cornell University). Cultures were maintained as described by Freedman and Gossett[1]. Headspace above culture was obtained for analysis. No internal standard was present.

Zero-valent iron system

100 ml Milli-Q water, 1.8 mg PCE, 400 μg n-pentane and 40 g Fe was added to 160 ml Serum vials under anaerobic conditions and sealed with Teflon-lined septa. Vials were rotated vertically (20°C) at 8 rpm for well mixed conditions. Sample was taken for analysis at 168 h. Sorption PCE and TCE onto the iron occurs and could be accounted for by using the sorption isotherms obtained by Burris *et al.*[8] in conjunction with their Henry's constants.

Vitamin B_{12}/titanium citrate system

100 ml Milli-Q water, 290 μg PCE, 67 μg n-pentane, 1.7 mg vitamin B_{12} and 150 mg titanium citrate was added to 160 ml serum vials under anaerobic conditions and sealed with Teflon-lined septa. Vials were maintained at 20°C. Sample taken for analysis at 2 h. Calibration standards using the same water and vapor volumes were used for quantitation (results not reported here).

RESULTS

A chromatogram of a standard containing the chlorinated ethenes and hydrocarbon gases using only the SP-1000/Carbopack B column is shown in Figure 2a. Separation of the chlorinated ethenes is accomplished, with the exception of the 1,2-DCE isomers which co-elute. The hydrocarbon gases are poorly resolved or unresolved near the void volume. A chromatogram of the same standard on the dual column system is shown in Figure 2b. The hydrocarbon gases are resolved on the dual column system with peak positions not interferring with those of the chlorinated ethenes.

The main parameter which affects hydrocarbon gas peak positions relative to those of the chlorinated ethenes is the length of the Carboxen 1000 column relative to the SP-1000 column. Trial and error is required to obtain a Carboxen 1000 column length which is suitable.

Table 1 gives method detection limits (MDL, as mass in water and vapor phases per vial) for the chlorinated ethenes and selected hydrocarbon gases in the dual column, sequence reversal gas chromatographic system with flame ionization detection using a 500 μl headspace injection volume. Since the samples and standards are water/vapor systems, these lower detection limits are specific to the system (i.e., 100 ml water volume and 60 ml headspace volume). This is due to the different Henry's constants for each component and the importance of the volumes of the two phases in the vapor/water partitioning relationship. This procedure (i.e., accounting for the Henry's constants within the calibration) for calibration standards and sample assays is convenient when studying transformations of these compounds in vapor/water systems. Relatively high sensitivity is obtained for most of the analytes due to the combination of the packed 1/8 inch columns and flame ionization detection.

Three different methods of reducing PCE were examined using the dual column, sequence reversal GC system to illustrate the versatility of the analytical method for different applications. PCE degradation in the zero-valent iron system is shown in Figure 3. The primary intermediates and products are TCE, acetylene, ethene and ethane. A series of unchlorinated C_3–C_5 compounds were also observed. PCE

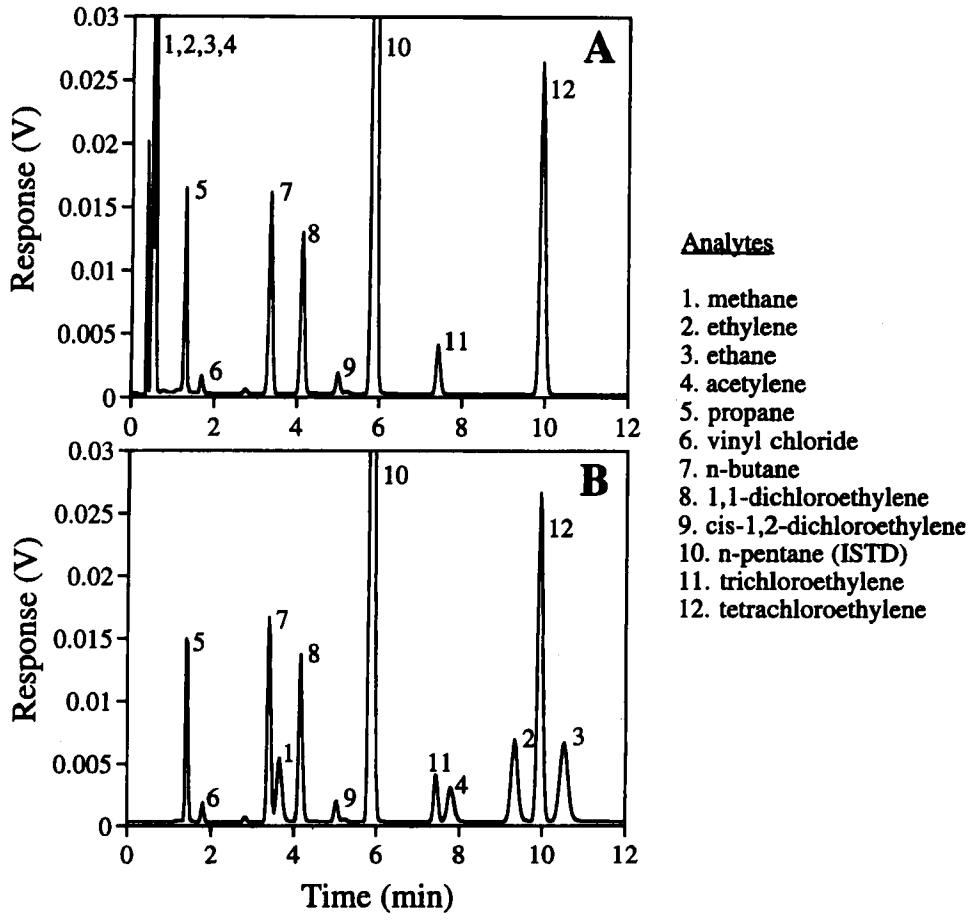

Figure 2 Chromatograms of standard containing chlorinated ethenes and selected hydrocarbon gases using: A – 8 ft × 1/8 in ss column packed with 1% SP-1000 on 60/80 Carbopack B only; and B – the dual column gas chromatography with column sequence reversal procedure as described in the text.

degradation in the vitamin B_{12} system is shown in Figure 4. The production of TCE, cis-1,2,-DCE and acetylene were observed. Figure 5 showns the degradation of PCE due to the anaerobic PCE-degrading microbial culture. Near complete conversion to vinyl chloride and ethylene is observed.

CONCLUSIONS

The dual column, sequence reversal GC method presented permits the detection of the primary products and intermediates for several reductive transformations of chlorinated ethenes in a vapor/water system. Calibration standards can be used to account for Henry's Law vapor/water partitioning. This GC procedure uses a single injector and a single detector which simplifies calibration and data interpretation. High sensitivity is

Table 1 Method detection limits (MDL)[a], relative response factors (RRF, n-pentane as internal standard) and retention times (RT) for tetrachloroethylene, trichloroethylene and selected compounds in a vapor/water system (160 ml sealed serum vial containing 100 ml H_2O and 60 ml headspace at 20°C) using the dual-column sequence reversal GC/FID procedure.

Compound	*RT (min)*	*RRF*	*MDL[a] (nmol)*
Propane	1.41	1.04E-1	2.3
Vinyl chloride	1.80	2.18E-2	0.5
n-Butane	3.41	1.51E-1	0.2
Methane	3.67	3.50E-2	1.4
1,1-Dichloroethylene	4.16	2.82E-2	0.9
cis-1,2-Dichloroethylene	5.01	6.00E-3	3.1
n-Pentane (ISTD)	5.88	1.00	b
Trichloroethylene	7.45	1.25E-2	9.1
Acetylene	7.81	2.28E-2	4.0
Ethylene	9.34	5.79E-2	7.0
Tetrachloroethylene	9.94	1.83E-2	29
Ethane	10.5	6.73E-2	6.7

[a] – based upon 500 µl headspace injection volume
b – not applicable

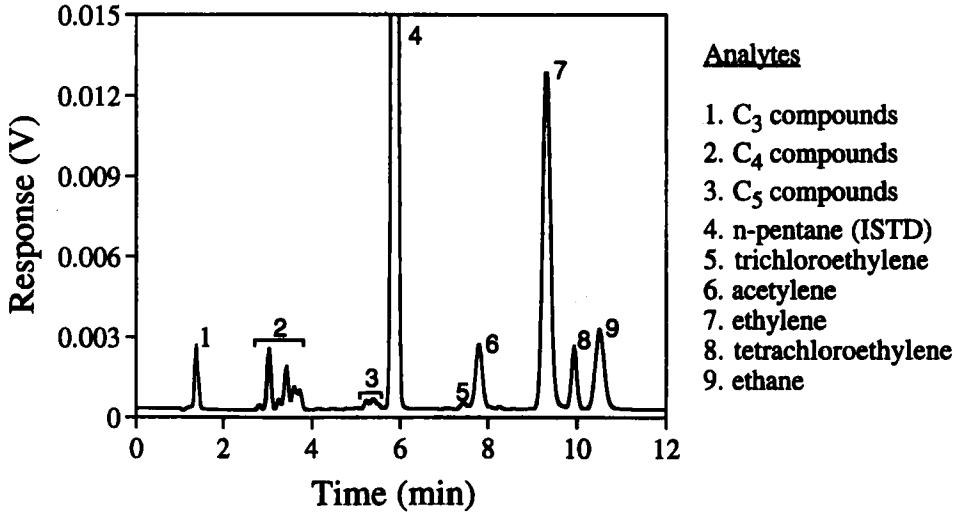

Figure 3 Chromatogram of PCE degradation in system containing zero-valent iron.

obtained for most of the analytes due to the combination of the packed GC columns and flame ionization detection. Simulaneous determination of the chlorinated ethenes and C_2 hydrocarbon gases is accomplished, which substantially facilitates pathway, mass balance and kinetic studies on reductive transformations of chlorinated ethenes. This method has proven efficient in terms of analysis time and equipment usage.

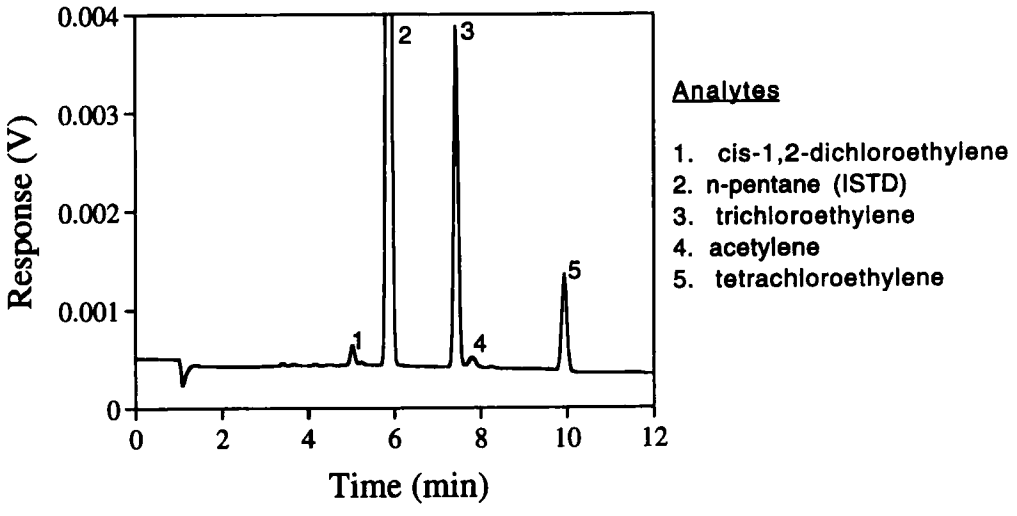

Figure 4 Chromatogram of PCE degradation in system containing vitamin B_{12} and titanium citrate.

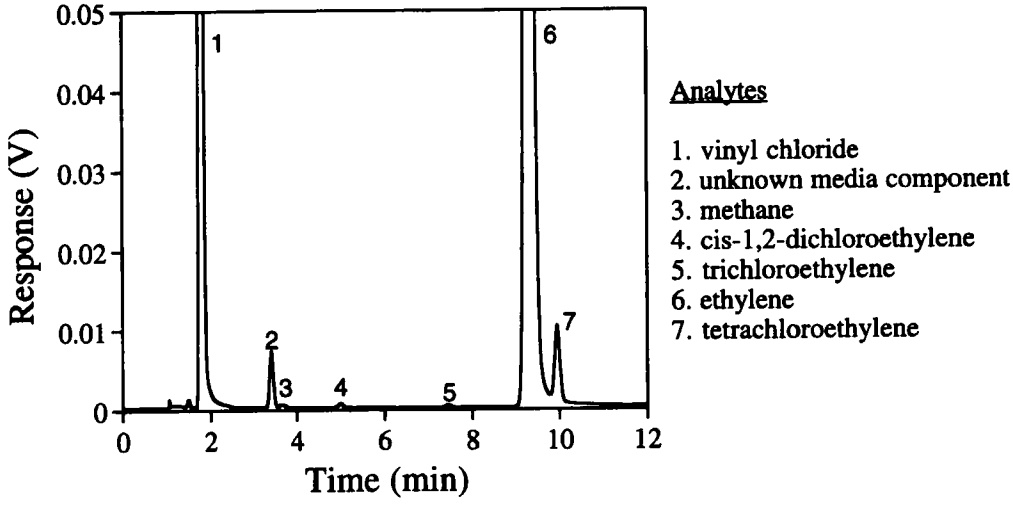

Figure 5 Chromatogram of PCE degradation in system containing anaerobic PCE-degrading microbial consortium (no n-pentane internal standard present).

Acknowledgements

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References

1. D. L. Freedman and J. M. Gossett, *Applied Environ. Microbio.*, **55**, 2144–2151 (1989).
2. W. P. de Bruin, M. J. J. Kotterman, M. A. Posthumus, G. Schraa and A. J. B. Zehnder, *Applied Environ. Microbio.*, **58**, 1996–2000 (1992).
3. C. J. Gantzer and L. P. Wackett, *Environ. Sci. Technol.*, **25**, 715–722 (1991).
4. R. W. Gillham and S. O'Hannesin, *Ground Water*, **32**, 958–967 (1994).
5. T. D. DiStefano, J. M. Gossett and S. H. Zinder, *Applied Environ. Microbio.*, **57**, 2287–2292 (1991).
6. D. E. Willis, *Anal. Chem.*, **50**, 827–830 (1978).
7. D. E. Willis, *J. Chromatogr. Sci.*, **24**, 417–422 (1986).
8. D. R. Burris, T. J. Campbell and V. S. Manoranjan, *Environ. Sci. Technol.*, **29**, 2850–2855 (1995).