ELSEVIER

Journal of Chromatography A, 677 (1994) 201–205

JOURNAL OF CHROMATOGRAPHY A

Short Communication

Analysis of the petroleum components benzene, toluene, ethyl benzene and the xylenes in water by commercially available solid-phase microextraction and carbon-layer open tubular capillary column gas chromatography

Leonard P. Sarna[a], G.R. Barrie Webster[a,*], Marcia R. Friesen-Fischer[b], Ramanathan Sri Ranjan[b]

[a]*Department of Soil Science, University of Manitoba, Winnipeg, MB R3T 2N2, Canada*
[b]*Department of Agricultural Engineering, University of Manitoba, Winnipeg, MB R3T 5V6, Canada*

First received 3 November 1993; revised manuscript received 8 March 1994

Abstract

Extraction of the petroleum components benzene, toluene, ethyl benzene and the xylenes (BTEX) from water is described using a commercially available poly(dimethylsiloxane) solid-phase microextraction fibre assembly with separation and quantification by carbon-layer open tubular capillary column gas chromatography and flame ionization detection. All components of BTEX are resolved. No cryofocussing is required.

1. Introduction

Contamination of surface and ground water with hydrocarbon fuel is an increasing problem. In both the monitoring of such contamination and in determining the success of remediation methods, a straightforward and inexpensive analytical method is required. Benzene, toluene, ethyl benzene and the three isomers of xylene (*o*-, *m*- and *p*-) (BTEX) are common industrial solvents and fuel components and were used in this study in view of their importance as common contaminants of ground water [1] as well as their reported presence in landfill leachates [2]. Their presence may be due to incomplete combustion of gasoline, leaking underground fuel-storage tanks, or accidental spills of gasoline or other types of hydrocarbon fuels, or industrial accidents.

Analytical methodology for these compounds usually involves liquid–liquid extraction [3,4], purge-and-trap [5,6] or headspace sampling [7] followed by capillary column gas chromatography (GC) using an appropriate detector, such as flame ionization detection (FID) or mass spectrometry (MS).

The new poly(dimethylsiloxane)-coated extraction fibre technique first reported by Belardi and Pawliszyn [8] has been successfully used to extract 2-naphthol from aqueous solution and further described in a series of recent papers [9–15]. Thermal desorption of the sorbed BTEX

* Corresponding author.

0021-9673/94/$07.00
SSDI 0021-9673(94)00442-C

within the GC injector coupled with cryofocussing was used in conjunction with conventional capillary GC and FID, or ion-trap detection. The technique has also demonstrated potential application to the extraction of chlorobenzenes and polychlorinated biphenyls [9], caffeine and fragrances [11] and US Environmental Protection Agency priority pollutants [13]. In each case, cryotrapping has been utilized to focus the more volatile analytes on the capillary column prior to analysis.

Theoretical considerations of the solid-phase microextraction technique (SPME) have been discussed thoroughly in the literature [9,10] and need not be repeated here, except to say that the amount of analyte absorbed by the coated fibre in a given time has been shown to be affected by three major factors: (a) the distribution constant of the analyte, (b) the volume of the stationary phase and (c) the stirring of the solution (which has been shown to shorten equilibration time). In SPME, exhaustive extraction does not occur. An equilibrium is established between the aqueous and stationary phases and it has been demonstrated that a linear relationship exists between the amount of analyte sorbed to the stationary phase and the concentration of analyte in the sample. This relationship is mathematically described in Eq. 1

$$n = KV_sC_{aq} \quad (1)$$

where n = number of moles of analyte absorbed by the stationary phase, K = distribution constant of the analyte, V_s = volume of the stationary phase and C_{aq} = concentration of the analyte in the aqueous phase.

Conventional capillary GC of BTEX has usually been carried out using non-polar columns, e.g., DB-1 and DB-5 columns (Chromatographic Specialties, Brockville, Canada) [16–18]. As mentioned above, use of these columns for SPME analysis has required cryofocussing following thermal desorption in the GC injector. Recently, GC analysis of the BTEX contaminants split-injected in the conventional manner has been reported using the recently developed carbon-layer open tubular (CLOT) capillary column [19,20] from Supelco (Canada) (Oakville, Canada). We report a simple, new method for the analysis of BTEX from aqueous samples in which the convenience of solventless fibre extraction is mated with the separating power of the CLOT column without the need for cryofocussing.

2. Experimental

2.1. Standards

Conventional standard solutions of benzene, toluene, ethyl benzene and the xylenes (0.002%, v/v) were made up in dichloromethane. Injections of 1.7 to 170 ng/μl of each component were used to plot a standard curve.

A standard solution in methanol of benzene, toluene, ethyl benzene and *o*-, *m*- and *p*-xylene (0.002%, v/v) was prepared for use in spiking of water samples at levels from 35 to 850 ng component per ml.

2.2. Extraction

SPME extraction was performed using a Supelco No. 5-7300 manual 100-μm poly(dimethylsiloxane) solid-phase microextraction fibre assembly. Aliquots of 10 ml of spiked water samples were placed in 12-ml screw-cap vials equipped with stir bars, fitted with silicone/PTFE septa, and clamped in place on a magnetic stir plate. The SPME assembly was clamped in place above and resting on the vial cap. The vial septum was pierced with the septum-piercing needle and the fibre was lowered into the solution so that the stainless-steel needle attachment was just below the meniscus (Fig. 1). After 2.0, 3.5 or 5.0 min extraction time, the fibre was retracted into the septum-piercing needle and the needle was withdrawn from the vial septum.

2.3. Injection

To determine the optimum depth of penetration for the fibre in the GC injection port, the needle/fibre assembly was compared to a normal 10-μl GC syringe. The length comprising the

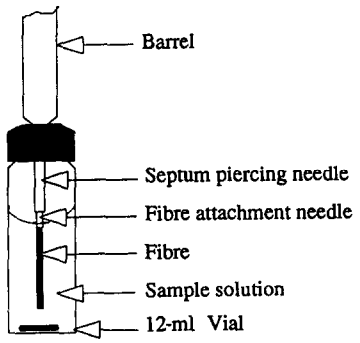

Fig. 1. Septum cap vial with SPME assembly illustrating position of fibre and septum-piercing needle during extraction. Small magnetic stir bar is shown.

stainless-steel septum-piercing needle plus the attachment needle and the silica fibre was adjusted to equal the length of a normal syringe needle. The SPME fibre assembly was adjusted to bring the top of the barrel to 3.4 cm on the scale on the fibre assembly.

The SPME fibre assembly was clamped upright over the GC injection port. The GC septum was pierced using the septum-piercing needle with the barrel of the fibre assembly resting on the GC injection port. The fibre was lowered into the injection port with the purge off. After 2 min desorption time, the fibre was retracted into the septum-piercing needle, the needle was withdrawn from the injection port, and the chromatography was begun.

The completeness of the thermal desorption was checked by carrying out "blank" runs of the previously desorbed fibre by GC using a thermal desorption time of 2 min.

2.4. Analysis

A Hewlett-Packard 5890 GC system equipped with FID and operating in the splitless mode was used for the analysis of the BTEX. Separations were conducted using a Supelco 30 m × 0.32 mm I.D. CLOT column. The chromatographic conditions were as follows: injector, 220°C; column, 40°C for 2 min, 15°C/min to 180°C, hold 1 min; detector, 250°C; flow-rates: helium carrier, 1.8 ml/min; helium makeup, 30 ml/min; hydrogen, 30 ml/min; air, 150 ml/min. SPME samples from BTEX solutions containing 35 to 850 ng/ml were analyzed and the FID responses related to the concentrations sampled.

3. Results and discussion

New analytical methodology based on a combination of the previously separately de-

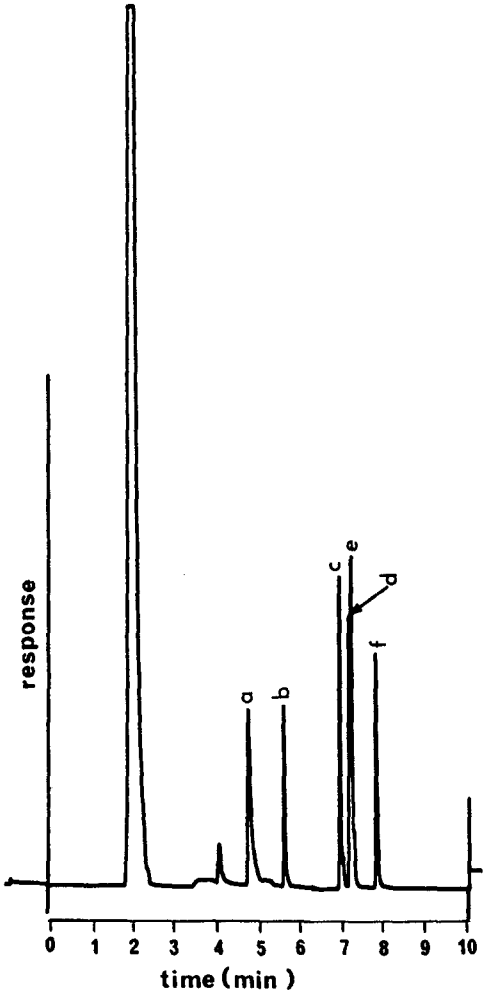

Fig. 2. Recovery of BTEX components from water sample spiked at 170 ng/ml by SPME–CLOT-GC–FID showing resolution of the *m*- and *p*-xylene isomers. Peak identities are given in Table 1. Unlabelled peaks prior to peak a, from the left, are methanol from the BTEX solutions used to spike the water, and an unknown. Total desorption and GC run time, 10 min.

scribed techniques of SPME and CLOT column capillary GC with FID has been successfully demonstrated to be feasible for the analysis of BTEX hydrocarbon contaminants in water. The apparatus for each of these techniques is now available "off the shelf".

Little difference in BTEX levels recovered was shown between the exposure times chosen, and is consistent with earlier reports [12,13]. While a 2-min extraction time was shown to be sufficient for BTEX from water followed by a 2-min thermal desorption time in the injection port of the GC, we chose 3.5 min exposure time for this work. Complete desorption after 2 min at 220°C was demonstrated. Total run time for a desorption and GC analysis was 10 min.

Fig. 2 demonstrates the recovery of BTEX components from a 10-ml aliquot spiked at 170 ng/ml per component. Two points are noteworthy. The first is that the chromatogram was generated without the need of the cryotrapping required for all previous work involving the use of SPME. Cryotrapping was previously required to minimize peak broadening associated with the relatively long desorption times involved in sample introduction by SPME. The second point is that the chromatogram clearly illustrates resolution of the *m*- and *p*-xylene isomers, not seen in earlier papers using either conventional or SPME analysis.

Since SPME relies on the partition of the BTEX from water into the polymer coating of the extraction fibre, the response seen for each component will vary according to its partition coefficient. Table 1 presents data on the retention time and minimum detectable limit for each of the BTEX components. The linearity of the response for each of the component compounds compared to its concentration in the spiked water sample was determined. The r^2 values in Table 1 reflect the goodness of fit over the range of 36 to 860 ng/ml of BTEX components in water. The differences in minimum detectable limits for the BTEX components more closely reflect the trend in the octanol–water partition coefficients (K_{ow}) reported by Arthur et al. [12] than the distribution coefficients in their original study and support their premise that the K_{ow} values of analytes can be used to predict the linear range and limit of quantification in new method development using these fibres before any experimental work is begun. The current study used the commercially supplied SPME fibre; Arthur et al. used fibres prepared in their own laboratory.

4. Conclusions

Analysis of BTEX in water by SPME, thermal desorption in the injection port, and GC–FID was directly possible using the commercially available CLOT column with linear response demonstrated for water samples containing 35 to

Table 1
Retention relative to benzene, minimum detectable limit (MDL) by direct fibre introduction of individual BTEX components from fortified water, and linear regression results (coefficient of determination) for the BTEX components extracted from water by SPME and desorbed and analyzed by GC

Compound	Relative retention	MDL (ng)	Range of fortification (ng/ml)	r^2
(a) Benzene	1.00	0.4	35–850	0.9507
(b) Toluene	1.34	0.4	35–850	0.9701
(c) Ethylbenzene	1.63	0.05	35–850	0.9930
(d) *p*-Xylene	1.68	0.2	35–850	0.9923
(e) *m*-Xylene	1.69	0.2	35–850	0.9904
(f) *o*-Xylene	1.81	0.1	35–350	0.9973

Benzene retention time was 4.18 min.

850 ng/μl. The previously prescribed cryofocussing of the desorbed BTEX is now unnecessary, making the SPME–CLOT column technique for BTEX readily usable by most analytical laboratories equipped with normal GC–FID instrumentation.

References

[1] D.M. Mackay, P.V. Roberts and J.A. Cherry, *Environ. Sci. Technol.*, 19 (1985) 384.
[2] J.F. Barker, *Water Pollut. Res. J. Canada*, 22 (1987) 33.
[3] G.A. Eiceman, J.T. McConnon, M. Zaman, C. Shuey and D. Earp, *Int. J. Environ. Anal. Chem.*, 24 (1986) 143.
[4] *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846*, US Environmental Protection Agency, 3rd ed., July 1992, method 3520A.
[5] S.B. Hawthorne and R.E. Sievers, *Environ. Sci. Technol.*, 18 (1984) 483.
[6] *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846*, US Environmental Protection Agency, 3rd ed., July 1992, method 5030A.
[7] J.F. Pankow, *Environ. Sci. Technol.*, 25 (1991) 123.
[8] R.P. Belardi and J. Pawliszyn, *Water Pollut. Res. J. Canada*, 24 (1989) 179.
[9] C.L. Arthur and J. Pawliszyn, *Anal. Chem.*, 62 (1990) 2145.
[10] D. Louch, S. Motlagh and J. Pawliszyn, *Anal. Chem.*, 64 (1992) 1187.
[11] S.B. Hawthorne, D.J. Miller, J. Pawliszyn and C.L. Arthur, *J. Chromatogr.*, 603 (1992) 185.
[12] C.L. Arthur, L.M. Killam, S. Motlagh, M. Lin, D.W. Potter and J. Pawliszyn, *Environ. Sci. Technol.*, 26 (1992) 979.
[13] C.L. Arthur, D.W. Potter, K.D. Bucholtz, S. Motlagh and J. Pawliszyn, *LC·GC*, 10 (1992) 656.
[14] D.W. Potter and J. Pawliszyn, *J. Chromatogr.*, 625 (1992) 247.
[15] C.L. Arthur, L.M. Killam, K.D. Bucholtz, J. Pawliszyn and J.R. Berg, *Anal. Chem.*, 64 (1992) 1960.
[16] P.V. Cline, J.J. Delfino and P.C.S. Rao, *Environ. Sci. Technol.*, 25 (1991) 914.
[17] S.R. Hutchins, *Environ. Toxicol. Chem.*, 10 (1991) 1437.
[18] S.R. Hutchins, G.W. Sewell, D.A. Kovacs and G.A. Smith, *Environ. Sci. Technol.*, 25 (1991) 68.
[19] P.S. Spock, R.E. Long and L. Sidisky, *Supelco Reporter*, XI, No. 4 (1992) 23.
[20] L.M. Sidisky and M.V. Robillard, *J. High Resolut. Chromatogr.*, 16 (1993) 116.