Journal of Chromatography, 642 (1993) 117–122
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2765

Trace determination of volatile organic compounds in water by enrichment in ultra-thick-film capillary traps and gas chromatography

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ABSTRACT

The technique by which volatile organic compounds are enriched in coated or uncoated capillaries, and desorbed for qualitative gas chromatographic determination, was adapted for quantitative analysis by using a 1-m length of ultra-thick-film trap (145-μm film thickness) to extract the volatile compounds flowing through the trap at 0°C. The trapped volatiles are thermally desorbed, cryotrapped on an analytical capillary column and determined by gas chromatography with flame ionization detection. It was found that analytes such as dichloromethane and chloroform did not break through when sampling 1 ml of water. With this sampling volume, relative standard deviations well below *ca.* 2% and *ca.* 2–4% were obtained for most of the analytes at levels of 1 ppm (v/v) and 1 ppb (v/v), respectively.

INTRODUCTION

The determination of low concentrations of volatile organic compounds in water and water-containing samples mostly requires a concentration step prior to gas chromatographic (GC) measurement. Concentration procedures include closed-loop stripping [1], open-loop or dynamic stripping, also known as purge-and-trap [2,3], and liquid–liquid extraction [4–6], which could conceivably contribute to environmental pollution owing to the relatively large volumes of halogenated solvents that are used in some applications. A simple, rapid and sensitive method that does not require a preconcentration step is the direct aqueous injection technique in conjunction with electron-capture detection (ECD) and/or flame ionization detection (FID) [7,8]. It has also been shown that trace components can be stripped from large aqueous samples passed through long, uncoated copper and polyethylene capillaries [9]. So far, however, this observation has not been implemented in a protocol for quantitative trace analysis.

Kaiser and Rieder [10] developed a qualitative method for the enrichment of high-boiling organic compounds in potable water by liquid–liquid enrichment in a polysiloxane-coated capillary column and Blomberg and Roeraade [11], having succeeded in coating glass capillaries with an ultra-thick polysiloxane stationary phase film, demonstrated the application of these thick-film capillaries to the qualitative analysis of organic compounds in water. Similar traps were produced in our laboratory by the insertion of a polysiloxane rubber tube into a fused-silica tube with 0.53 mm I.D. to produce traps with a film or lining thickness of 145 μm [12]. The finished product had an I.D. of 0.24 mm. It was found that these traps can be applied very successfully to the qualitative analysis of airborne organic volatiles [12–14] and apolar organic compounds in aqueous samples. Although it was demonstrated [15] that the full thickness of the polysiloxane rubber lining of these traps is utilized to retain volatile compounds, it was found that small and highly volatile compounds are not retained very effectively on

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0021-9673/93/$06.00

traps short enough to be subjected to thermal desorption in the injector of the gas chromatograph. These observations also apply to the extraction of volatile organic compounds from aqueous samples. The use of longer traps and the trapping of volatiles at subambient temperatures therefore seemed to be unavoidable, even though traps longer than about 70 mm would require additional equipment for the desorption of the volatiles. As far as the analysis of airborne volatiles is concerned, reasonably accurate information on the breakthrough volumes of volatile compounds can be obtained by the extrapolation of the results achieved with shorter traps. However, no information is available on the influence of parameters such as temperature and flow-rate on the efficiency with which organic compounds are extracted from water by an ultra-thick-film capillary trap.

The main aim of our research on the application of capillary traps to the GC determination of volatile organic compounds is to make technology and procedures available that would enable any normally equipped analytical or quality control laboratory to make at least a preliminary or emergency assessment of problems arising from the presence of organic contaminants in, for example, air of gas samples, beverages, drinking water or process effluents, without having to invest in expensive instrumentation or time-consuming conversions of existing equipment. In this paper we report the results of experiments carried out to determine the scope and limitations of long ultra-thick-film traps for the trace determination of organic volatiles in aqueous samples.

EXPERIMENTAL

Long (1-m) fused-silica open-tubular traps were produced by inserting polysiloxane rubber tubing (0.65 mm O.D. × 0.30 mm I.D.) (Silastic medical grade tubing; Dow Corning, Midlands, MI, USA) into polyimide-coated fused-silica tubes (0.70 mm O.D. × 0.53 mm I.D.) according to the procedure described by Burger *et al.* [12] to give ultra-thick-film traps of 0.24 mm I.D. and with a film or lining thickness of 145 μm. Several traps were connected in series, installed in a GC oven and conditioned at 280°C for 80 h.

A spiked water sample containing dichloromethane, chloroform, bromoform, tetrachloroethylene, benzyl chloride, heptane, benzene, toluene, *p*-xylene, and *p*-cymene at the 1 ppm (v/v) level was prepared by injecting 10 μl of a mixture of these compounds through a PTFE-backed septum into the vortex of 1 l of magnetically stirred purified water (obtained with a Milli-Q system; Millipore, Bedford, MA, USA) in a 1-l round-bottomed flask, the neck of which was shortened to leave a relatively small headspace volume (sample A). Water obtained from the Milli-Q system contained a large number of organic compounds at a level of <10 ppb and had to be stripped of these interfering compounds by boiling away about 50% of the original volume. A water sample containing the above-mentioned analytes at a level of 1 ppb (v/v) (*p*-cymeme 2 ppb) was prepared by adding, according to the previously described procedure, 1 ml of a freshly prepared 1 ppm sample to 999 g of this purified water (sample B).

Two ultra-thick-film traps, installed in capillary column cages, were connected with shrinkable PTFE tubing. Using shrinkable PTFE tubing, 0.5- and 1.2-m lengths of fused-silica tubing (0.53 mm I.D.) were connected to the inlet end of the first trap and the oulet end of the second (guard) trap, respectively. The connected traps were immersed into an ice–water bath and purified water was sucked through the traps until all air bubbles had been purged from the trap. This normally took only a few minutes. The outlet end of the fused-silica extension was closed by inserting it into a silicone-rubber septum, whereafter the inlet end was inserted through a septum or an opened stopcock into the spiked water sample. Water was allowed to flow through the traps for 1 h, about 1 ml of water being collected in a weighed vial. The outlet end of the fused-silica extension was again closed and the inlet end removed from the water sample, then the septum was removed from the outlet end of the tubing and the contents of the traps and extensions were allowed to siphon to waste. The water collected in the vial during the first part of the experiment was carefully weighed and represented the total volume of water sampled in the experiment. To achieve the specified flow-rate the tip of the outlet extension had to be *ca.* 85 cm below the surface of the water in the inlet reservoir.

The guard trap was installed in the first oven of a

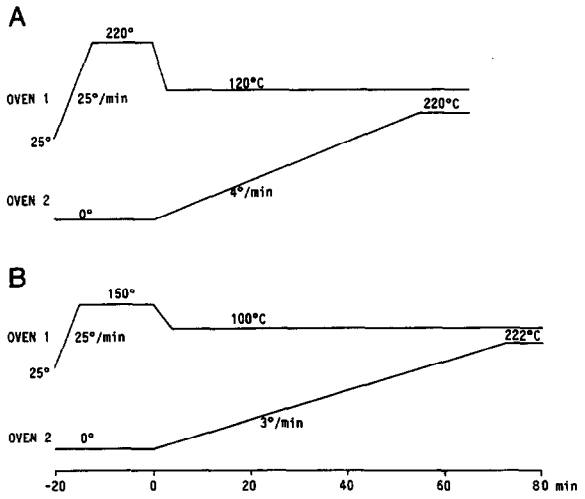

Fig. 1. Temperature programmes used for the desorption and analysis of volatile organic compounds in water. (A) Determination of analytes in sample A at a level of 1 ppm; (B) determination of analytes in sample B at a level of 1 ppb.

Siemens Sichromat 2 gas chromatograph. The volatile organic compounds were thermally desorbed and transported by the carrier gas (helium at 35 cm/s) to an analytical capillary column (40 m × 0.3 mm I.D., glass, coated with immobilized PS-255 with a film thickness of 5 μm) installed in the second oven. The two ovens of the gas chromatograph were temperature programmed according to the profiles depicted in Fig. 1. After it had been established that no breakthrough to the second (guard) trap had taken place, the first trap was subjected to a similar desorption and analysis procedure. Quantification of the FID response was done with a Hewlett-Packard Model 3385A integrator.

Direct on-column, aqueous injection of water containing the analytes at a level of *ca.* 1 ppm was carried out with a Carlo Erba Model 5300 gas chromatograph fitted with a cold on-column injector and a glass capillary column (40 m × 0.3 mm I.D.) coated with PS-255 with a film thickness of 5 μm and connected to a 10 m × 0.32 mm I.D. deactivated fused-silica retention gap.

RESULTS AND DISCUSSION

As far as solubility in water and extractability by the apolar trap lining are concerned, no internal standard can be expected to behave exactly like analytes such as the smaller halogenated compounds. It is therefore clear that the only way to achieve reproducible quantitative results is to employ conditions that ensure quantitative extraction of all the analytes. This requires a relatively low flow-rate of the water through the trap. A flow-rate of *ca.* 1 ml/h was chosen for this purpose. Although this may seem to be excessively time consuming, it must be kept in mind that several traps can be loaded simultaneously and then stored for analysis at a later stage, or that two traps can be used in a loading-and-analysis cycle in an automated system.

The extraction of analytes from water by the polysiloxane lining of a trap cannot be compared with the almost irreversible adsorption of organic molecules on an activated charcoal trap. With ultra-thick-film traps breakthrough is generally not due to overloading or saturation of the traps, but to the movement of the analyte molecules through the trap by normal chromatographic processes. Although the increased rate of mass transfer at higher temperatures would have allowed the use of higher flow-rates, the limiting factor in this method is the relatively low capacity of the trap for the more volatile analytes. Taking the results of studies on temperature-programmed liquid chromatography [16] into consideration, sampling was carried out at the lowest possible temperature (0°C) to increase the capacity of the trap. A series of analyses were carried out with water spiked with the analytes at concentrations of *ca.* 1 ppm. It was found that breakthrough of dichloromethane became detectable at a sampling volume of *ca.* 2 ml. This means that dichloromethane cannot be quantitatively extracted and retained in the trap when sample volumes larger than about 2 ml are used. As the main aim of this study was the development of a method for volatile water contaminants including dichloromethane, further determinations were carried out with sample volumes of about 1 ml.

The results obtained with water containing the ten analyte compounds at a level of 1 ppm are given in Table I and a typical gas chromatogram is shown in Fig. 2A. The relative standard deviations (R.S.D.s) of the absolute peak areas are fairly good, especially if it is taken into consideration that the integration system used does not allow any manipulation of the accumulated data, such as baseline adjustment. For comparison of these results with

TABLE I

AREA COUNT REPEATABILITY FOR THE ANALYSIS OF WATER CONTAINING ORGANIC COMPOUNDS AT A CONCENTRATION OF *ca.* 1 ppm (SAMPLE A) (n = 5)

Compound	Average uncorrected area counts[a]	Standard deviation	R.S.D. (%)
Dichloromethane	72 468	954	1.32
Chloroform	34 088	138	0.41
Benzene	253 328	3333	1.32
Heptane	39 652	9348	23.58
Toluene	233 146	2224	0.95
Tetrachloroethylene	91 448	1380	1.51
Benzyl chloride	231 860	1199	0.52
p-Xylene	230 420	10 334	4.49
Bromoform	5397	982	18.20
p-Cymene	184 619	1253	0.68

[a] Attenuation: 100×2^8.

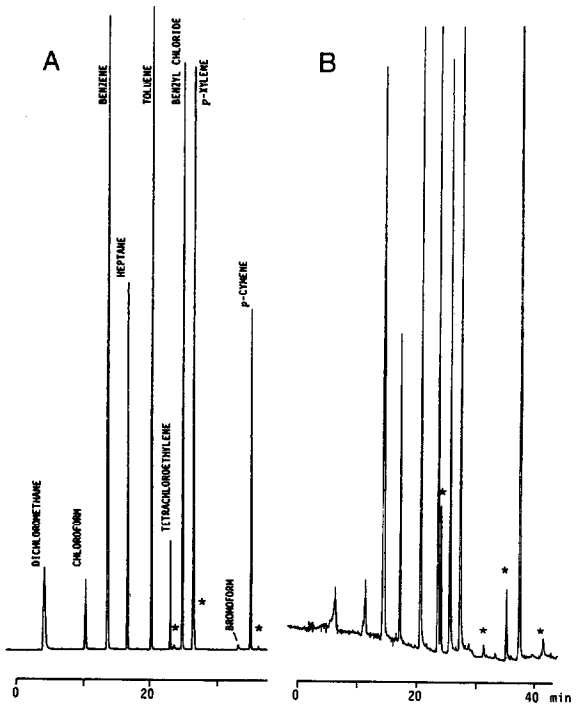

Fig. 2. Typical gas chromatograms of volatile organic compounds extracted from water samples in a 1-m ultra-thick-film trap. Water samples containing the analytes at levels of (A) 1 ppm and (B) 1 ppb. GC conditions as described under Experimental and in Fig. 1. Asterisks indicate artefacts and/or contaminants.

those obtainable with direct aqueous injection [7], 5 μl of a spiked water sample containing the analytes at a level of *ca.* 1 ppm were injected on-column into an apolar column fitted with a 10-m retention gap. With such relatively small injection volumes and FID, the determination of these analytes at a level of 1 ppb was found to be out of the reach of the direct injection method.

The exceptionally high R.S.D. for heptane in Table I is the result of steadily decreasing area counts over the five days during which the determinations at the 1 ppm level were made. Owing to its low solubility in water, this compound probably became concentrated in the headspace gas, resulting in a decrease in its concentration in the water. It is impossible to preserve the integrity of water samples spiked at these levels for longer than 1–2 days at the most. The results in Table I were nevertheless used here to illustrate the effect that storage of samples may have on the accuracy and reproducibility of results. This problem was found to be less pronounced at the 1 ppb level. The large R.S.D. for bromoform can be ascribed to the low FID response to this compound, resulting in a larger effect of integration errors on the area counts obtained for bromoform than for other analytes having normal FID responses. The relatively high R.S.D. obtained for *p*-xylene can be ascribed to the incomplete separation of this compound from an impurity, probably a cyclosiloxane produced by thermal decomposition of the polysiloxane lining of the trap. To avoid this problem in analyses at lower concentration levels, the desorption temperature was lowered from 220 to 150°C, which still gave complete desorption of all the compounds, and the programming rate was changed from 4 to 3°C/min.

At the 1 ppb level, the low molar response factors of the halogenated compounds resulted in poorer R.S.D.s. It was found to be impossible to determine bromoform with its very low response factor at a level of 1 ppb. The results of an area count reproducibility study are given in Table II. A typical gas chromatogram obtained at a level of 1 ppb is shown in Fig. 2B.

As dichloromethane and possibly also chloroform cannot be substantially enriched by using larger volumes of the water sample, it does not seem to be feasible to determine these compounds at concentrations much below 100 ppt with the present

TABLE II

AREA COUNT REPEATABILITY FOR THE ANALYSIS OF WATER CONTAINING ORGANIC COMPOUNDS AT A CONCENTRATION OF *ca.* 1 ppb (SAMPLE B) (n = 5)

Compound	Average uncorrected area counts[a]	Standard deviation	R.S.D. (%)
Dichloromethane	8817	802	9.10
Chloroform	5433	690	12.70
Benzene	35 488	1414	3.98
Heptane	32 721	1452	4.44
Toluene	71 624	525	0.73
Tetrachloroethylene	118 748	2340	1.97
Benzyl chloride	76 560	1834	2.40
p-Xylene	148 395	3150	2.12
p-Cymene	350 720	10 751	3.07

[a] Attenuation: 1×2^6.

method, in conjunction with FID. If ECD is employed, however, these compounds should be readily detectable at a level of 1 ppt. As far as the compounds with larger molar response factors are concerned, acceptable R.S.D.s were obtained without having to increase the volume of water siphoned through the trap, although the more favourable partition coefficients of the higher compounds allow larger volumes of water to be passed through a trap before breakthrough occurs. However, at such low levels the collection of reliable quantitative data was hampered by residual impurities in the water used for the preparation of spiked water samples and especially by the thermal decomposition products of the polysiloxane rubber lining of the trap. If appropriate precautions are not take, the accumulation of polisiloxane decomposition products can lead to the appearance of large interfering peaks, even in analyses at the 1 ppb level. It was found to be essential to cool the trap relatively slowly to at least 120°C before the analytical column is cooled for the next analysis. The trap is also left at the desorption temperature only long enough to effect quantitative desorption of the analytes in question. If these precautions are not observed, strongly tailing decomposition product peaks are produced which might overlap with, or obscure, the peaks of the analytes.

CONCLUSIONS

Although it cannot be claimed that ultra-thick-film traps are universally applicable to the determination of all volatile organic compounds in any type of water sample, the method described in this paper could bring the determination of certain water contaminants within reach of laboratories without ECD instrumentation, provided that instrumentation is available for the thermal desorption of analytes from the trap (double-oven gas chromatograph or ohmic heating) and cryofocusing of the desorbed volatile compounds. Depending on the R.S.D. that is considered acceptable, it is possible to determine the more volatile organic halides at levels of, for example, 1–10 ppb and the results reported here can serve as guidelines for the development of methods for the determination of similar compounds. Interference of artefact peaks produced by the decomposition of the polysiloxane trap lining can cause problems when less volatile compounds have to be determined at levels of 1 ppb or lower. However, the xylenes, *p*-cymene, etc., did not break through when 10 ml of water were sampled and the problem resulting from the increasing size of artefact peaks that are formed when desorption temperatures have to be increased to achieve relatively rapid and quantitative desorption of high-boiling compounds can therefore be offset by sampling larger volumes of water, allowing higher attenuation values to be used. General guidelines will have to be established for the determination of such higher boiling compounds as far as the flow-rate at which these compounds can be extracted from water and the temperature and time required for complete desorption from the trap are concerned.

REFERENCES

1 K. Grob, *J. Chromatogr.*, 84 (1973) 255.
2 A. Zlatkis, H. A. Lichtenstein and A. Tishbee, *Chromatographia*, 6 (1973) 67.
3 T. A. Bellar and J. J. Lichtenberg, *J. Am. Water Works Assoc.*, 66 (1974) 739.
4 F. Dietz and J. Traud, *Wasser*, 41 (1973) 137.
5 K. Grob, K. Grob, Jr. and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
6 M. C. Goldberg, L. Delong and M. Sinclair, *Anal. Chem.*, 45 (1973) 89.

7 Z. Zlatkis, F.-S. Wang and H. Shanfield, *Anal. Chem.*, 55 (1983) 1848.
8 K. Grob and A. Habich, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 6 (1983) 11.
9 A. Zlatkis, S. Weisner and L. Ghaoui, *Chromatographia*, 21 (1986) 19.
10 R. E. Kaiser and R. Rieder, *J. Chromatogr.*, 477 (1989) 49.
11 S. Blomberg and J. Roeraade, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 457.
12 B. V. Burger, M. le Roux and W. J. G. Burger, *J. High Resolut. Chromatogr.*, 13 (1990) 777.
13 B. V. Burger, A. E. Nell and W. G. B. Petersen, *J. High Resolut. Chromatogr.*, 14 (1991) 718.
14 B. V. Burger and W. G. B. Petersen, *Z. Naturforsch. C: Biosci.*, 46 (1991) 1073.
15 B. V. Burger and M. le Roux, *J. High Resolut. Chromatogr.*, 15 (1992).
16 J. S. Yoo, J. T. Watson and V. L. McGuffin, *J. Microcol. Sep.*, 4 (1992) 349; and references cited therein.