Purge-and-trap injection capillary gas chromatographic determination of volatile aromatic hydrocarbons in river sediment

P. Kuráň, R. Kubinec, I. Ostrovský, L. Soják*

Chemical Institute, Faculty of Natural Sciences, Comenius University, Mlynská Dolina CH-2, 84215 Bratislava, Slovak Republic

Abstract

Dynamic headspace and purge-and-trap with methanolic extraction techniques for the simple and rapid determination of trace amounts of volatile aromatic hydrocarbons in river sediments were compared. The purge-and-trap technique with metanolic extraction using an external standard method gives a better representativeness of the analysed sample, a twofold higher precision and twofold lower detection limits. When the internal standard method is applied, the precision of both methods increases 3–4 times and the detection limits decrease 4–5 times.

1. Introduction

Water and sediment are two matrices closely related to each other in a water column. The determination of organic pollutants in water and sediment samples has been intensively studied during last two decades [1]. Many methods for the determination of organic compounds in ground and surface waters have been described but their direct application to the determination of volatile organic compounds (VOCs) in inland water sediments is infrequent. The water column consists of two phases, the aqueous phase and suspended solids, which complicate their sampling and analysis. It is necessary to take into account factors such as the particle size distribution of the sediment, the content of organic carbon and the considerable composition variability of various types of sediments. In the

determination of VOCs, the loss of volatile components during sampling and sample handling and the representativeness of the collected sample should be considered. Available techniques for the determination of volatiles allow results of varying quality, and require validation of the applied methods [2].

Proper sampling is a necessary condition for obtaining reliable analytical results. The sediments represent dynamic systems and therefore the results of every sediment analysis are related to the time of sampling.

The treatment of the collected sediment is usually a critical stage of analysis. It is time consuming and represents the greatest source of errors in environmental analysis [3,4].

The most frequent techniques used for the determination of volatiles are headspace methods [5,6] and purge-and-trap methods [7,8,9] that can be employed in various arrangements. For the static headspace method, the analyte

* Corresponding author.

concentrations are not changed after achieving equilibrium. This equilibrium is only disturbed during sampling before injection. The technique is simple and undemanding with regard to instrumentation, but its disadvantage is the relatively low sensitivity. In the dynamic headspace method, the gaseous phase over the sample is permanently purged with carrier gas, which carries the analytes to the trapping medium. This technique enables lower detection limits to be achieved [1]. It is possible to determine the solutes with a lower vapour pressure and the possibility of contamination from the septum is removed. The quality of a representative sample can be improved by modifying these techniques with extraction of volatiles from sediment with a suitable solvent. When methanol is used as the solvent, the microbial degradation of the contaminants is suppressed by its toxic effects. The possibility of the loss of very volatile compounds and the possibility of contamination of the extract are solved by minimizing the free space over the solvent [2,7].

The dependence of the accuracy of analytical results on the solid matrix type can differ. In the analysis of VOCs in solid matrices [5,10] this dependence was not observed and for this reason it is possible to employ a simple external standardization method. However, in the determination of gasoline constituents in different soil types, such a dependence of the results obtained on the matrix type was found [2].

The purpose of this work was to compare dynamic headspace and purge-and-trap injection with metanolic extraction (PTI/MeOH) techniques for the determination of trace amounts of volatile aromatic hydrocarbons at the ppm level in river sediments from the point of view of reliability of the results (precision, reproducibility and recovery).

2. Experimental

2.1. Purge-and-trap unit

The PTI device (Chrompack, Middelburg, Netherlands) was used as an automatic stripping and preconcentration system. This unit is designed for the isolation and preconcentration of volatiles from liquid matrices. This device allows the simultaneous connection of one capillary column to two parallel detectors.

The PTI unit consisted of a 5-ml stripping vessel, a water condenser cooled with ethanol, a fused-silica capillary column (30 cm × 0.53 mm I.D.; film thickness 2.65 μm) coated with an immobilized methylsilicone stationary phase (SE-54) and an oven that heats the trapping capillary tube.

2.2. Gas chromatograph

A CP 9000 gas chromatograph (Chrompack) was used. The separation was carried out using a fused-silica capillary column (25 m × 0.32 mm I.D.; film thickness 0.52 μm) with SE-54 as the stationary phase. The column was connected to a flame ionization detector by means of a metal coupling and a 30 cm length of capillary of 0.32 mm I.D.

The oven temperature was maintained at 40°C for 7 min, then programmed at 10°C/min to 240°C. After reaching the final temperature, the analysis was completed. Nitrogen (99.999% purity) (MG Tatragas, Bratislava, Slovak Republic) was used as the carrier gas.

2.3. Reagents and standards

Drinking water was used for dilution of the methanolic extract.

A standard mixture of volatile aromatic hydrocarbons (benzene, 3.5 mg/kg; toluene, 3.5 mg/kg; ethylbenzene, 6.9 mg/kg; m-xylene, 6.9 mg/kg; o-xylene, 6.9 mg/kg) was prepared from analytical-reagent grade chemicals (Lachema, Brno, Czech Republic) by dilution with methanol.

2.4. Dynamic headspace method

A 1-g amount of the wet sediment was spiked with 4 μl of the standard mixture of volatile aromatic hydrocarbons. The sample was heated in a water-bath (70°C) and purged with nitrogen

(99.999%) at 30 ml/min. The volatiles were trapped in the SE-54 (2.65 μm) fused-silica capillary column (30 cm × 0.53 mm I.D.) cooled to −100°C. After 10 min the capillary was heated to 220°C. Subsequently, the volatiles were desorbed into the SE-54 (0.52 μm) analytical capillary column (25 m × 0.32 mm I.D.).

2.5. Purge-and-trap with methanolic extraction method

A 1-g amount of the wet sediment was spiked with 4 μl of the standard mixture, then 1 ml of methanol was added and the mixture was shaken for 2 min in a closed vessel. A 100-μl volume of the extract was transferred into 5 ml of drinking water, which was immediately purged at 30°C for 10 min. The other analytical parameters were the same as for the dynamic headspace method.

3. Results and discussion

The possibilities of using the Chrompack purge-and-trap injector, designed for the determination of volatiles in waters, in the determination of volatile aromatic hydrocarbons in sediments using the dynamic headspace and the PTI/MeOH techniques were studied. As model compounds benzene, toluene, ethylbenzene, m-xylene and o-xylene were used with the aim of

finding the optimum experimental conditions for their simple and rapid determination at the ppm level.

3.1. Influence of spiking procedure on response

The influence of the location of adding pollutant to the sediment on the response and reproducibility was studied. A considerable difference in the results obtained by the dynamic headspace and PTI/MeOH methods was observed when the surface and the bottom layer of the sediment were spiked with the standard mixture. The differences in the responses of the peak areas of the analytes from seven successive analyses for these two extreme positions of pollutant addition are documented in Table 1. It can be seen that the peak areas of aromatics in the dynamic headspace method are approximately double for sediment spiked in the surface layer. This result is related to the better contact of the purge gas with analytes spiked on the surface. In the PTI/MeOH method this effect, despite a ca. tenfold lower response, is considerably suppressed and the peak areas of aromatics are on average about 20–30% higher (with the exception of benzene). The relative standard deviations confirm the elimination of this effect because they are virtually independent of the position of pollutant addition.

This experiment basically simulates heteroge-

Table 1
Peak areas of standard aromatic hydrocarbons and their relative standard deviations for the different procedures of sediment spiking for dynamic headspace (under 70°C) and PTI/MeOH (under 30°C) techniques

Aromatic hydrocarbon	x_p				R.S.D. (%)			
	Dynamic headspace		PTI/MeOH		Dynamic headspace		PTI/MeOH	
	1	2	1	2	1	2	1	2
Benzene	15 451	47 666	2133	4225	85.0	35.3	41.8	21.1
Toluene	17 892	44 509	6044	8435	88.1	26.2	36.7	11.1
Ethylbenzene	47 708	100 905	5202	7178	92.1	27.3	29.4	19.9
m-Xylene	50 998	105 929	5533	7513	89.4	26.9	26.9	19.7
o-Xylene	56 673	115 116	6074	7889	83.4	26.1	22.0	18.2

x_p = average peak area (n = 7); R.S.D. = relative standard deviation; 1 = bottom layer spiked with standard; 2 = surface spiked with standard.

Table 2
R.S.D.s and detection limits (DL) for standard aromatic hydrocarbons added to the sediment using the external standard method
with the dynamic headspace (under 70°C) and PTI/MeOH (under 30°C) techniques

Aromatic hydrocarbon	Dynamic headspace			PTI/MeOH		
	x_p	R.S.D. (%)	DL (mg/kg)	x_p	R.S.D. (%)	DL (mg/kg)
Benzene	31 558	70.1	7.4	3457	36.4	3.8
Toluene	31 201	61.6	6.5	7427	28.6	3.0
Ethylbenzene	74 307	60.2	12.5	6190	28.3	5.0
m-Xylene	78 464	59.0	12.3	6523	26.9	5.6
o-Xylene	85 894	56.6	11.7	6953	24.4	5.1
Average	–	61.5	10.1	–	28.9	4.5

x_p = average peak area ($n = 14$); R.S.D. = relative standard deviation.

neous sediments and indicates the parameter that influences the results of the analysis.

3.2. External and internal standardization methods

A comparison of the precisions and detection limits for the external and internal standardization methods without taking into account the influence of the spiking procedure is presented in Tables 2 and 3.

In a real analysis of a sediment, especially a heterogeneous one, it is not possible to predict the position of a pollutant in the sediment. The final result in the dynamic headspace technique will contain an error depending on the pollutant position. This is why it is necessary to evaluate results obtained for both extreme positions as one set, and hence it is possible to approach the closest to the real situation.

The values in Table 2 indicate that in the PTI/MeOH method the precision of peak areas is approximately twice that for the dynamic headspace method (average R.S.D. 28.9% vs. 61.5%), which indicates the elimination of the effect of the pollutant position. The detection limits, calculated on the basis of average peak areas of aromatics and their standard deviation for 99% probability (the coefficient of the Student distribution for 13 degrees of freedom is $t = 3.01$), are ca. 50% lower for the PTI/MeOH technique (4.5 vs. 10.1 mg/kg).

Table 3
R.S.D.s and detection limits (DL) for standard aromatic hydrocarbons added to the sediment using the internal standard method
with the dynamic headspace (under 70°C) and PTI/MeOH (under 30°C) techniques

Aromatic hydrocarbon	Dynamic headspace			PTI/MeOH		
	x_p	R.S.D. (%)	DL (mg/kg)	x_p	R.S.D. (%)	DL (mg/kg)
Benzene	42.86	39.1	4.1	54.66	14.0	1.5
Toluene	41.89	18.8	2.0	123.08	20.8	2.2
Ethylbenzene	100.00	–	–	100.00	–	–
m-Xylene	107.08	3.2	0.7	106.07	3.3	0.7
o-Xylene	120.40	7.7	1.6	114.13	7.0	1.5
Average	–	17.2	2.1	–	11.2	1.5

x_p = average peak area ($n = 14$); R.S.D. = relative standard deviation.

Table 4
Recoveries of standard aromatic hydrocarbons from sediment using the dynamic headspace (under 70°C) and PTI/MeOH (under 30°C) techniques

Aromatic hydrocarbon	Dynamic headspace			PTI/MeOH		
	x_p	R.S.D. (%)	Recovery (%)	x_p	R.S.D. (%)	Recovery (%)
Benzene	145 163	45.7	21.7	16 694	16.8	20.7
Toluene	140 690	24.4	22.2	19 745	20.4	37.6
Ethylbenzene	263 725	14.8	28.2	22 359	15.8	27.6
m-Xylene	269 175	14.2	29.1	22 224	15.6	29.4
o-Xylene	264 792	11.3	32.3	21 066	15.5	33.0
Average	–	22.1	26.7	–	16.8	29.7

x_p = average peak area (n = 7); R.S.D. = relative standard deviation.

Despite the increased precision of the analysis by using the PTI/MeOH method, the relative standard deviations were still relatively high (see Table 2). Therefore, the possibilities of increasing the precision of the method by using ethylbenzene as an internal standard were studied. Both methods were again compared. The average peak areas of particular aromatics with the corresponding relative standard deviations and detection limits are given in Table 3. They were recalculated with respect to the area of ethylbenzene as an internal standard (=100). In this case the precision of the PTI/MeOH method was on average 11.2% and for the dynamic headspace method 17.2%; the detection limits were 1.5 mg/kg on average for the PTI/MeOH method and 2.1 mg/kg for the dynamic headspace method. The precision of both methods in comparison with results obtained from the external standard method increased approximately 3–4 times and simultaneously the detection limits were decreased approximately 4–5 times. It is concluded that the results obtained by the two techniques are comparable.

3.3. Recoveries of volatile aromatics from sediment

The recoveries of aromatics from sediment are given in Table 4. They are relatively low for both
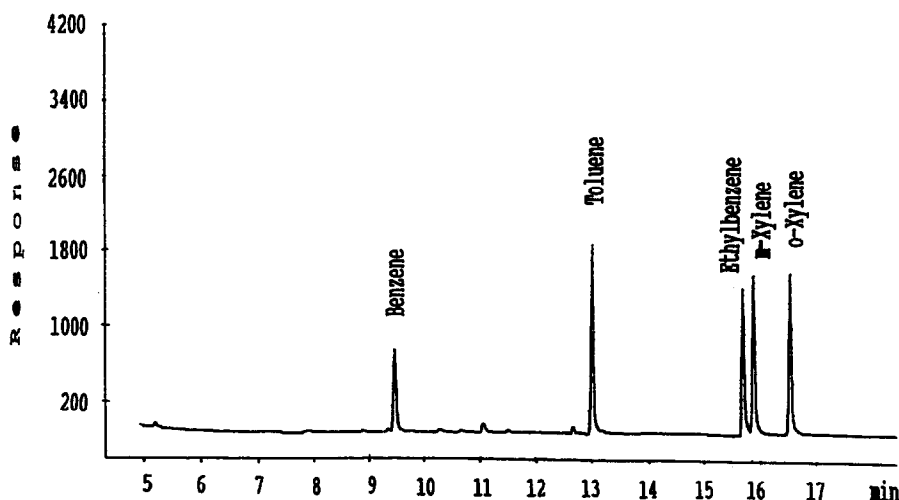

Fig. 1. Chromatogram of the standard mixture of volatile aromatic hydrocarbons in a sediment analysed by the PTI/MeOH method.

the dynamic headspace and PTI/MeOH techniques (on average 26.7% and 29.7%, respectively). The low recoveries are related to the short purging times in both methods in order to decrease time and economics of the analyses. The recovery of aromatics increases moderately with decreasing volatility. This finding is contradictory to results presented in the literature [1], where it was stated that the recovery decreases with increasing boiling point. The problem of the recovery increase and detection limit decrease will be studied further.

The results obtained were employed for the determination of volatile hydrocarbons in sediments and sludges by means of the PTI/MeOH technique. A chromatogram of the standard mixture is shown in Fig. 1.

4. Conclusions

Dynamic headspace and PTI/MeOH techniques for the determination of volatile aromatic hydrocarbons in river sediment from the point of view of precision, sensitivity, representativeness of the analysed sample and recovery were compared. The PTI/MeOH method with an external standard gives a better representativeness of the analysed portion and a twofold higher precision

and twofold lower detection limits. When the internal standard method is applied, the precision of both methods increases 3–4 times and the detection limits decrease 4–5 times. The results obtained for the two techniques with the internal standard method are comparable. The disadvantage of both methods is the low recovery of aromatics from sediment.

5. References

[1] A.P. Bianchi, M.S. Varney and J. Philips, J. Chromatogr., 542 (1991) 413.
[2] J.L. Parr, G. Walters and M. Hoffman, in P.T. Kostecki and E.J. Calabrese (Editors), Hydrocarbon Contaminated Soils and Groundwater, Vol. 1, Lewis, MI, 1991, p. 105.
[3] R.E. Majors, LC · GC, 4 (1992) 10.
[4] C.L.P. Thomas, LC · GC, 6 (1992) 9.
[5] A. Venema, J. High Resolut. Chromatogr., 13 (1990) 537.
[6] M. Tóth and H.R. Buser, J. Chromatogr., 598 (1992) 303.
[7] J.V. Hinshaw, LC · GC, 3 (1990) 22.
[8] R.P. Eganhouse, T.F. Dorsey and C.S. Phinney and A.M. Westcott, J. Chromatogr., 628 (1993) 81.
[9] S.A. Rounds and J.F. Pankow, J. Chromatogr., 629 (1993) 321.
[10] A. Hagman, Ph.D. Thesis, University of Stockholm, Stockholm, 1988, p. 7.