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Note

Quantitative evaluation of a simple dynamic headspace analysis technique for non-polar pollutants in aqueous samples at the ng/kg level

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The theoretical and practical aspects of the various modes of headspace analysis have been reviewed by Drozd and Novák[1] and, more recently, by Núñez *et al.*[2]. In this paper we report some quantitative data obtained with the purge-and-trap technique. The aqueous sample solution is purged with pure nitrogen. The analytes are collected in a Tenax trap. The trap tube is mounted to the injection port of a gas chromatograph. The analytes are thermally desorbed, and concentrated as a narrow band at the top of a capillary column that is cooled with liquid nitrogen. Thereafter, the analytes are separated and detected with a flame ionization detector. This simple off-line mode has been described by several workers[3,4], and is attractive because of its low costs and applicability to any modern gas chromatograph. Since quantitative results (recovery and repeatability data) are rather scarce and, as far as we know, not yet given at the ng/kg level, we carefully examined each of the above-mentioned procedure steps for a number of alkanes, alkylbenzenes and some chlorinated ethenes. To this aim, we analysed distilled water, natural ditch water, and a soil–water suspension spiked with known amounts of these solutes. Recovery data, larger than theoretically predicted, will be explained. It will be shown that quantitation at the ng/kg level includes the proper choice of a reference compound and internal standards, and the elimination of carry-over effects due to incomplete desorption of the analytes and due to a slight deterioration of Tenax TA. Finally, the possibilities and the limitations of this type of purge-and-trap method will be discussed.

EXPERIMENTAL

Chemicals, standard and sample solutions, gas purification, and trap adsorbent

n-Alkane, benzene and alkylbenzene standards were supplied by Chrompack (Middelburg, The Netherlands), and the chlorinated ethenes by Merck (Darmstadt, F.R.G.). Stock solutions of these standards in methanol were stored at −20°C, and had a shelf-life of at least one month. The spike solutions prepared from the stock solutions, were used within two days. The most volatile standards (heptane and the

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chloroethenes) showed a decrease of concentration of *ca.* 1%/h. This is accounted for in the calibration method described below. Methanol was chosen as the solvent in order to avoid interference with early eluting analyte peaks in the gas chromatogram. Sample solutions were prepared in the strip vessel by injection of a known amount of spike solution below the level of the stirred water at ambient temperature. All experiments were carried out with 900 ml of distilled water or ditch water, and with 800 ml of distilled water containing 25 g of wet sandy soil (19.5 g of dry soil). The ditch water was taken from a non-industrialized peat soil area, appearing to be free of the examined solutes, and had a total organic carbon content (TOC) of 65 mg/l. The dry soil had an organic matter content of 7% and appeared to contain traces of toluene and *o*-xylene. Matrices with a rather large organic matter content were chosen to establish the influence on the analysis results.

Nitrogen (technical grade) was purified with a gas-clean filter set (Chrompack), and used as the purge gas, the carrier gas, and the make-up gas.

Tenax TA (60–80 mesh, Chrompack) was used as the trap adsorbent. It has a specific surface area of 19–30 m^2/g, and is thermally stable up to at least 250°C (these data apply to Tenax GC[2], which is believed to have similar characteristics).

Apparatus and procedure

The strip vessel (22 cm × 7.4 cm I.D.) was equipped with a septum cap for the injection of the spike solutions, a short connection tube to a heated glass tube (or a cooler), and an inlet for the stripping gas. The gas entered the sample solution through a fine-porosity glass frit near the bottom of the vessel. The solution was homogenized with a magnetic stirrer to enlarge the residence time of the fine gas bubbles in the solution. The glass tube was thermostated at 100°C, and the cooler (used in the final experiments) at 20°C. Forss *et al.*[5] have shown that such a cooler does not noticeably affect the passage of the stripped solutes. All glassware was thoroughly cleaned and stored in an oven at 100°C until use.

The stainless-steel trap tube contained 1.2 g of Tenax TA, which is enough to prevent breakthrough of the examined solutes[6,7]. A flow-rate of 30 ml/min for the purge gas appeared to be optimal, as for bubble size. Stripping was carried out at 85°C for 60 min (except when stated otherwise). Details of the analysis procedure are presented in Table I. The purge of the Tenax trap after collection of the analytes is necessary to remove adsorbed water and methanol, which will cause plugging of the capillary column during solute focusing in the cold trap. Thermal desorption of the analytes from the Tenax was carried out with a home-made tube oven. The trap was connected to the capillary column in such a manner that the analytes were back-flushed into the column. The desorption temperature was regulated with a thermostat and measured with a copper–constantan thermocouple. During the desorption step, the gas chromatography oven was kept at −20°C with a stream of liquid nitrogen through the perpendicular part of a glass Tee. Its straight part surrounded the top of the capillary column to give a temperature gradient of −36°C/cm in the gas flow direction. Adverse effects by aerosol formation were not apparent. The analyses were carried out with a Kipp 8200 gas chromatograph, equipped with a linear temperature programmer and a flame ionization detector, and a Varian CDS 401 integrator. The solutes were separated on a WCOT fused-silica Sil 5 CB capillary (50 m × 0.23 mm I.D.), supplied by Chrompack. The make-up flow was 30 ml/min. A plate number

TABLE I

EXPERIMENTAL CONDITIONS FOR THE COMPLETE ANALYSIS PROCEDURE APPLIED IN THE FINAL EXPERIMENTS (RESULTS GIVEN IN TABLE III)

Analysis step	*t (min)*	*F (ml/min)*	*T(°C)*
Purge-and-trap step			
Nitrogen purge	60	30	85
Cooler and Tenax trap			20
Purge of Tenax trap	25	30 (off-line)	20
Desorption and focusing step			
Cooling of GC oven	10	0.16	20→ −20
Heating of desorption oven	10	0.24	20→350
Isothermal desorption	15	3.0	350
Separation step			
Programming of GC oven	70	0.36	−20→150
Regeneration step			
Regeneration of Tenax trap	20	60 (off-line)	350

of 4000/m was obtained for nonane, indicating that the solute focusing step is efficient.

The thermal stability of Tenax TA at the conditions specified in Table I was examined by analysing distilled water. The result is presented in Fig. 1a. Repeat experiments gave similar patterns with similar peak retention times, but variable peak heights. A chromatogram of spiked distilled water is given in Fig. 1b for comparison. The peaks denoted by T are believed to be due to deterioration of the Tenax by a combined action of heat and traces of trapped water. The T peaks do not interfere with solute peaks, except with those of benzene and toluene if present at the ng level.

The efficiency of the thermal desorption was examined by repeating only the desorption/cold trapping step after an analysis of spiked distilled water, keeping the Tenax trap *in situ*. The chromatogram is given in Fig. 1c. Obviously, decane and stronger-retained alkanes are not completely desorbed at 350°C, but T peaks are not apparent anymore (indicating that in the absence of water the thermal stability of Tenax TA in excellent indeed). The occurrence of a benzene peak in Fig. 1c is not expected. It may be due to slow diffusion of traces of benzene trapped in the micropores of the Tenax. To overcome the problem of incomplete desorption, we included a regeneration step in the procedure (see Table I), which appeared to suffice, and applied calibration with internal standards to obtain unbiased results.

RESULTS AND DISCUSSION

To eliminate bias due to the instability of some spike solutions in methanol, the standard solutions were directly injected into the Tenax tube and further analysed (DIA experiments), whereas the water and soil–water suspensions were analysed by the whole purge-and-trap procedure in close succession with the former DIA cali-

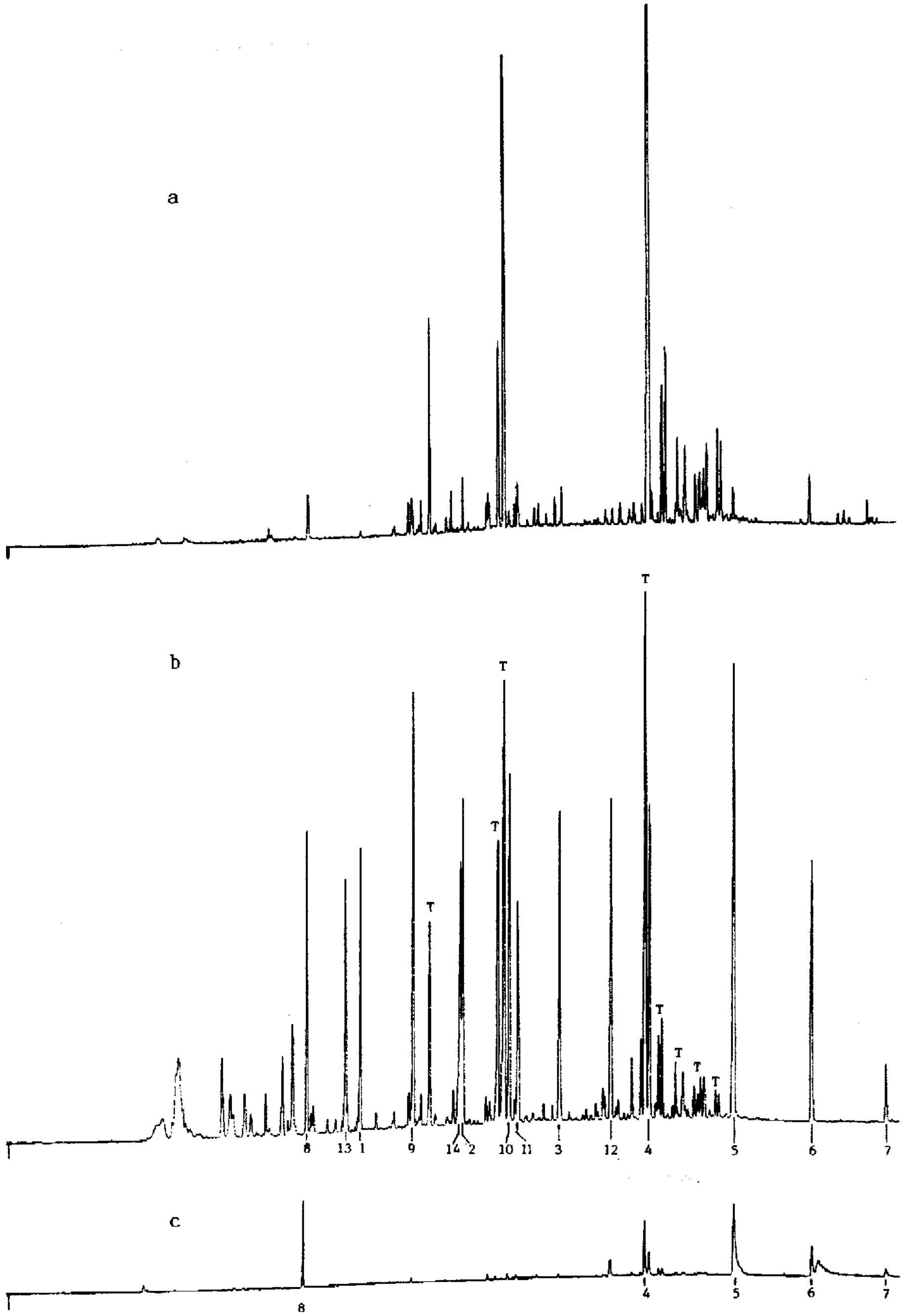

Fig. 1. (a) Chromatogram of unspiked distilled water, after purge-and-trap analysis. (b) Chromatogram of spiked distilled water. The solute code is given in Table III. The peaks denoted by T are believed to be due to deterioration of Tenax by a combined action of traces of trapped water and heat (*cf.* Fig. 1a). (c) Chromatogram obtained after repeated thermal desorption from the Tenax trap tube.

bration experiments. The dry vessel instrument calibration, proposed by Warner and Beasly[8], is not applicable in our work because it is based on the assumption of complete thermal solute desorption. In DIA experiments, the standards were injected via a conventional heated injection port with a gas inlet to flush the solution into the Tenax bed and to remove the solvent. To correct for the variability of injected volumes of spike solutions, all peak areas were normalized to that of nonane. Nonane proved to be a good reference compound because its spike solution appeared to be stable, it gave a straight calibration plot that passed through the origin (complete thermal desorption), and appeared to be completely recovered from distilled water and ditch water samples. DIA and purge-and-trap analysis results were reproducible within *ca.* 10%, which is acceptable at the ng/kg level.

In some preliminary experiments, it was examined whether ideal equilibium was attained in the strip vessel at 25°C and a purge flow of 30 ml/min. Recovery data are presented in Table II (last column) at a purge time of 20 min. Theoretical estimates for the recoveries can be obtained from the equation

$$Y(\%)/100 = [n_{i,w}^0 - n_{i,w}(t)]/n_{i,w}^0 = 1 - \exp[-Ft/(V_g + \mathrm{n}_w RT/H_{i,w})] \qquad (1)$$

which is readily derived from the mass balance equation, and is essentially similar to that proposed by Novák *et al.*[2]. In eqn. 1, $n_{i,w}^0$ and $n_{i,w}(t)$ are the numbers of moles

TABLE II

LITERATURE DATA FOR SOLUTE PRESSURES p_i^0, ACTIVITY COEFFICIENTS IN WATER $\gamma_{i,w}^\infty$, HENRY COEFFICIENTS $H_{i,w}$, AND CALCULATED AND EXPERIMENTAL RECOVERY DATA Y AT 25°C AND SOLUTE CONCENTRATIONS OF ABOUT 100 ng/kg (PRELIMINARY EXPERIMENTS)

Solute	*ln* $p_i^{0\star}$ *(ref. 9)*	*ln* $\gamma_{i,w}^\infty$ *(ref. 10)*	*ln* $H_{i,w}^\star$	$Y_{calc.}$ *(%)***	$\bar{Y} \pm s_Y$ *(%)*
n-Alkanes					
Heptane	1.81	14.46	16.27	100	95 ± 9
Octane	0.63	16.08	16.71	100	92 ± 3
Nonane (ref.)	−0.56	17.55[9]	16.99	100	(100)
Decane	−1.74	18.88[9]	17.14	100	86 ± 5
Dodecane	−4.15	21.70[9]	17.55	100	94 ± 2
Alkylbenzenes					
Benzene	2.54	7.79	10.33	14	19 ± 31
Toluene	1.34	9.17	10.51	16	24 ± 6
Ethylbenzene	0.24	10.49	10.73	20	24 ± 3
o-Xylene	−0.13	10.44	10.31	13	22 ± 7
Mesitylene	−1.11	11.85	10.74	20	29 ± 3
Chlorinated ethenes					
Trichloroethene	2.29	8.80[9]	11.09	27	
Tetrachloroethene	0.91	10.44	11.35	33	

* p^0 and H have the dimension kPa; $\gamma_{i,w}^\infty \geq 2500$.

** Theoretical estimates for Y were obtained from eqn. 1 with the data: Ft = 600 ml, V_g = 50 ml, and n_w = 50 mol.

of analyte i in the aqueous sample before equilibration with the purge gas and after a purge of t min, respectively. V_g is the gas volume (ml) in the vessel, and n_w is the number of moles of water to be sampled. F is the flow-rate of the purge gas (ml/min), R is the gas constant ($R = 8314.4$ ml kPa/mol K), T is the absolute temperature (K), and $H_{i,w}$ is the Henry coefficient (kPa). For sparingly soluble, liquid solutes $H_{i,w}$ is given by

$$H_{i,w} = p_i/x_{i,w} = p_i^0/x_{i,w}\,(\text{sat.}) = p_i^0\gamma_{i,w}^{\infty} \tag{2}$$

In this equation, p_i and $x_{i,w}$ are the vapour pressure and the mole fraction of i in the aqueous sample, respectively, under equilibrium conditions, and p_i^0 and $x_{i,w}$(sat.) are the vapour pressure of pure i and the mole fractional solubility of i in water, respectively. The latter is inversely proportional to the activity coefficient of i, $\gamma_{i,w}^{\infty}$, provided $x_{i,w}$(sat.) is smaller than 0.001. Experimental data for p_i^0, $\gamma_{i,w}^{\infty}$ and $H_{i,w}$ are given in columns 2, 3 and 4 of Table II, respectively.

Comparison of experimental and calculated recoveries in Table II shows that equilibrium is approximately attained under the applied conditions. The experimental recoveries for the alkylbenzenes appear to be larger than the predicted ones. This inconsistency may be explained by assuming that, besides transport via the gas phase, solute molecules are transferred to the gas above the water sample when they are adsorbed to the gas–water interface of the gas bubbles. Adsorption of non-polar pollutants to the air–water interface is a well-known phenomenon.

It is clear from Table II that alkylbenzenes and the examined chloroethenes cannot quantitatively be recovered under the present experimental conditions. It can be estimated from eqn. 1 that at 25°C *ca.* 19 l of purge gas are necessary to obtain a recovery of 99% for benzene. In general, such large gas volumes are not recommened because of the enhanced risk of breakthrough of volatiles in the Tenax trap. As salting-out effects appear to be smal[11], the best approach to enlarge $H_{i,w}$ is to increase the temperature of the sample solution during the purge step. From excess free energies for solutions of benzene in water[12] and vapour pressure data, it can be estimated that $\ln H_{i,w} = 12.86$ for benzene at 85°C. At this temperature, benzene can be recovered in quantities of up to 98% from 900 ml of water with a nitrogen purge of 30 ml/min for 1 h. At this high temperature, the heated glass tube connection between the vessel and the trap has to be replaced by a cooler flushed with tap-water, in order to prevent a large amount of water from entering the Tenax trap. Under these conditions, the final results were obtained (during a period of about six months). They are collected in Table III and give rise to the following remarks.

The reproducibility of the relative retention times, α, is sufficient for peak identification, except for octane and tetrachloroethene when only one of them would be present in the sample. The resolution of peaks 2 and 14 in Fig. 1b is large enough for quantitation.

Quantitative recoveries are obtained for the examined alkanes and alkylbenzenes in distilled water and ditch water, but for the chlorinated ethenes the results are less satisfactory. The average error estimate for a single analysis is *ca.* 12%, which is acceptable for environmental analysis results at the ng/kg level. Poor recoveries are obtained for spiked soil–water suspensions (results for toluene and *o*-xylene should be kept out of consideration, as the soil contained traces of these compounds).

TABLE III

RELATIVE RETENTION TIMES $\bar{\alpha}$ FOR VARIOUS SOLUTES FROM DISTILLED WATER (A), NATURAL DITCH WATER (B) AND SOIL–WATER SUSPENSIONS (C), SPIKED WITH ABOUT 100 ng OF SOLUTE

Mean data are given for n analyses; experimental conditions are given in Table I.

Solute	*Code*	$\bar{\alpha} \pm s_\alpha$	$\bar{Y} \pm s_Y$ (%)		
		$n = 36$	*A*	*B*	*C*
			$n = 6$	$n = 3$	$n = 3$
n-Alkanes					
Heptane	1	0.633 ± 0.015	100 ± 11	95 ± 12	82 ± 7
Octane	2	0.822 ± 0.006	105 ± 9	99 ± 10	74 ± 5
Nonane (ref.)*	3	1.000	(100)	(100)	64 ± 1
Decane	4	1.166 ± 0.006	101 ± 9	103 ± 9	38 ± 7
Undecane	5	1.322 ± 0.012	101 ± 11	109 ± 3	20 ± 5
Dodecane	6	1.472 ± 0.013	104 ± 19	116 ± 14	
Tridecane	7	1.610 ± 0.014	99 ± 12	105 ± 14	
Alkylbenzenes:					
Benzene	8	0.536 ± 0.015	94 ± 22	111 ± 12	52 ± 4
Toluene	9	0.732 ± 0.014	107 ± 23	96 ± 14	122 ± 7
Ethylbenzene	10	0.906 ± 0.006	90 ± 4	96 ± 2	76 ± 5
o-Xylene	11	0.921 ± 0.003	100 ± 7	104 ± 6	104 ± 10
Mesitylene	12	1.095 ± 0.005	101 ± 6	107 ± 10	75 ± 5
Chlorinated ethenes		$n = 12$	$n = 3$	$n = 1$	$n = 3$
Trichloroethene	13	0.608 ± 0.011	80 ± 13	73	60 ± 3
Tetrachloroethene	14	0.815 ± 0.008	92 ± 19	87	68 ± 6

* The retention time of *n*-nonane is equal to 37.9 ± 1.1 min. Quantitative recovery of nonane from spiked distilled and ditch water is obtained (see text).

For the series of alkanes, the logarithm of the adsorbed fraction (*i.e.* $1 - Y/100$) appears to be linearly related to the number of carbon atoms in the alkanes. This results points to strong adsorption to, and slow desorption from, the humic material in the soil. Because the distribution of organic matter in soil usually shows significant site-to-site variations, purge-and-trap sampling is not a suitable technique for the analysis of soil samples. It is worth noting that solute solubilization by soluble humic material in ditch water does not adversely affect the recoveries for the solutes examined.

The applicability of the open headspace sampling technique under the present conditions appears to be restricted to analytes with a Henry coefficient similar to that of benzene, or larger. From the H data collected by Mackay and Shiu[9], it can be concluded that the following classes of solutes obey this requirement: alkanes (with a carbon number $n_c \leqslant 14$, see also the recent results bu Curvers *et al.*[13]), alkylcyclopentanes and alkylcyclohexanes, alkenes and alkynes, alkylbenzenes, but only some of the halogenated alkanes and alkenes. The latter class of compounds can be sampled with a closed-loop headspace technique, using a metal bellow pump for the circulation of the purge gas, as has been shown by Narang and Bush[14]. This conclusion also provides a guideline for the selection of a suitable reference compound, after screening of the sample for possible pollutants. If necessary, a standard-addition calibration can be carried out[1].

Using a flame ionization detector, the detection limits for the alkanes and alkylbenzenes, and for the examined chlorinated ethenes are 1 and 5 ng/kg, respectively. These data are, for practical reasons, based on a detector response equal to ten times the noise level. This sensitivity amply suffices in pollution studies on these compounds. The use of 100-ml samples will be appropriate in many instances and is recommended in view of a proportional reduction of the required purge time. When more strip vessels and traps are used simultaneously, the analysis time per sample can be reduced to the GC analysis time (*ca.* 2 h in this work), which makes off-line purge-and-trap sampling suitable for serial analysis.

REFERENCES

1 J. Drozd and J. Novák, *J. Chromatogr.*, 165 (1979) 141.
2 A. J. Núñez, L. F. González and J. Janák, *J. Chromatogr.*, 300 (1984) 127.
3 A. B. Robinson, D. Partridge, M. Turner, R. Teranishi and L. Pauling, *J. Chromatogr.*, 85 (1973) 19.
4 W. Bertsch, E. Anderson and G. Holzer, *J. Chromatogr.*, 112 (1975) 701.
5 D. A. Forss, V. M. Jacobsen and E. H. Ramshaw, *J. Agric. Food Chem.*, 15 (1967) 1104.
6 R. H. Brown and C. J. Purnell, *J. Chromatogr.*, 178 (1979) 79.
7 J. Janák, J. Růžičková and J. Novák, *J. Chromatogr.*, 99 (1974) 689.
8 J. M. Warner and R. K. Beasley, *Anal. Chem.*, 56 (1984) 1953.
9 D. Mackay and W. Y. Shiu, *J. Phys. Chem. Ref. Data*, 10 (1981) 1175.
10 W. E. Hammers, G. J. Meurs and C. L. de Ligny, *J. Chromatogr.*, 246 (1982) 169.
11 M. M. Thomason and W. Bertsch, *J. Chromatogr.*, 279 (1983) 383.
12 W. E. Hammers and P. B. A. Verschoor, *J. Chromatogr.*, 282 (1983) 41.
13 J. Curvers, Th. Noy, C. Cramers and J. Rijks, *J. Chromatogr.*, 289 (1984) 171.
14 R. S. Narang and B. Bush, *Anal. Chem.*, 52 (1980) 2076.