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POSSIBILITIES AND LIMITATIONS OF DYNAMIC HEADSPACE SAMPLING AS A PRE-CONCENTRATION TECHNIQUE FOR TRACE ANALYSIS OF ORGANICS BY CAPILLARY GAS CHROMATOGRAPHY

J. CURVERS, Th. NOY, C. CRAMERS and J. RIJKS*

Eindhoven University of Technology, Department of Chemistry, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven (The Netherlands)

SUMMARY

   The possibilities, the limitations and the quantitative performance of dynamic headspace sampling, in particular closed-loop stripping, were investigated for various classes of organic substances in aqueous samples with concentrations down to the parts per 10^{12} (ppt) level. The effects of variations of some process factors (*e.g.*, the gas–liquid distribution coefficient, the sample temperature, the stripping gas volume and the type of solvent) on the recovery were studied. The experimental results of this study agree fairly well with those predicted by a theoretical model. The recovery is shown to be independent of concentration in a wide range of concentrations (200 ppt–20 ppb). For components that do not interact strongly with water, overall recoveries corresponding to a standard deviation of 10–15% are found. A detection limit of 10 ppt and enrichment factors up to 5000 can easily be obtained for non-polar components with boiling points up to 350°C for a 1-l sample.

INTRODUCTION

   Various methods and devices for trace enrichment have been described. Unfortunately, little has been reported on the evaluation and comparison of these methods and systems for different classes of substances and concentration levels. Therefore, an extensive study of the performance of various methods for isolating or concentrating trace amounts of organic compounds with sufficient volatility for capillary gas chromatographic (GC) analysis was started in our laboratory a few years ago.
   Recently we presented an extensive study[1] of the effect of various process factors on the recovery of steam distillation/extraction for components with wide ranges of volatility, polarity and concentration. In this paper we report on a similar study for "dynamic headspace sampling" (DHS). Dynamic headspace sampling is the continuous removal of the headspace vapour above a liquid or solid sample by means of a gas flow with subsequent trapping of the sample components by adsorption or cold trapping. The technique was introduced in the early 1960s by Swinnerton *et al.*[2,3]. In the literature all kinds of applications using different instrumental set-ups

can be found. Possibly the most powerful is the closed-loop stripping technique described by Grob[4]. Using only a small amount of charcoal as the sorbent and a related small volume of extraction solvent, concentrations as low as 0.1 ppt were determined.

This study was directed towards the effects of several experimental factors such as extraction solvent, stripping gas volume and temperature on the recovery and process rate in DHS. Model mixtures, covering a wide range of volatilities, functional groups and concentrations, were used for this purpose.

EXPERIMENTAL

Stock solutions of synthetic mixtures

The following stock solutions were prepared:

(1) "multimix", a mixture which contains substances with different functional groups, *e.g.*, alcohols, ketones, aromatics, with boiling points between 111 and 223°C and with a concentration of about 1% (w/v) per component;

(2) "hydrocarbon-mix", a mixture of normal hydrocarbons with carbon numbers ranging from 7 to 26, boiling points between 98 and 400°C and concentrations of about 100 ppm (w/v);

(3) "phenolic-mix", a mixture of phenol and mono- and dimethyl-substituted phenols with boiling points between 180 and 225°C and concentrations of about 0.2% (w/v) per component.

Equipment for DHS

A schematic representation of the quipment is shown in Fig. 1. As can be seen, it is almost equivalent to the closed-loop stripping devices according to Grob and Zürcher[5]. Real closed-loop experiments could not be performed, however, because of the contaminants released by the (inexpensive) pump (KNF No. 22.AN.18, membrane pump; Verder, Vleuten, The Netherlands). A clean-up filter (4) was placed between the pump (5) and the sample flask (1) in order to remove impurities in the
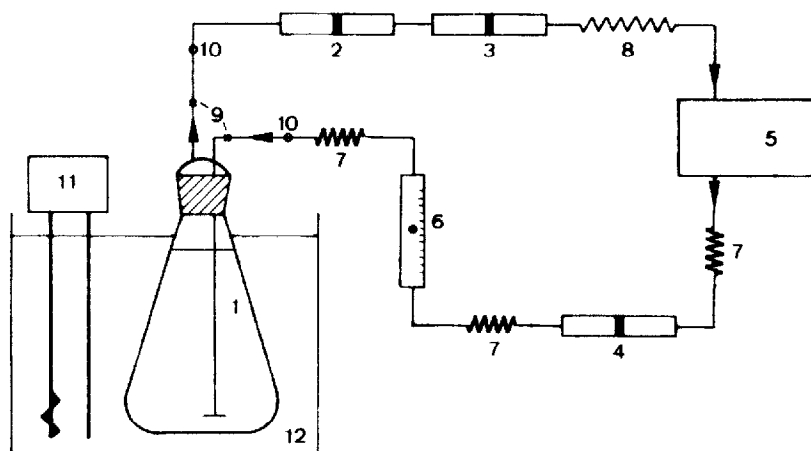

Fig. 1. Schematic design of the closed-loop stripping equipment. 1, Sample flask; 2, sample adsorption filter; 3, breakthrough filter; 4, clean-up filter; 5, pump; 6, flow meter; 7, coiled metal tubing; 8, capillary resistance; 9, spherical glass joints; 10, metal–glass connection; 11, heater/stirrer; 12, water-bath.

stripping gas. The clean-up filter and the adsorption filters (2, 3) were filled with charcoal (Aktivkohle für Gaschrom. nach Dr. Grob, 0.05–0.1 mm; Dr. Bender and Dr. Hobein AG, Zürich, Switzerland); no special pre-treatment was used.

The adsorption filters were constructed of glass tubing according to Fig. 2. The charcoal was positioned between two glass frits (porosity 30–50 μm, thickness 0.5 mm, outer diameter 3.8 mm). The inner diameter of the glass tubing was adjusted to the diameter of the frits in order to prevent losses of charcoal particles. After the frits had been placed in position the glass tube was slightly constricted just above the second frit to keep the filter discs in position. Two adsorption filters were placed in series behind the sample flask, the first to adsorb the stripped organics and the second to check whether breakthrough of the first had occurred.

Procedure

The sample flask is filled with 1 1 of doubly distilled water and placed in a water-bath for about 15 min to reach the desired temperature. An appropriate volume (a few microlitres) of one of the stock solutions is added by means of a syringe, below the water level. The flask is immediately stoppered and placed in the closed circuit. To avoid leakage the ground-glass joints are wetted with doubly distilled water and secured with clips. The glass joints have to be rewetted every 30 min. The stripping procedure is started by recirculating a volume of laboratory air of about 200 ml, with a flow rate of 300–350 ml/min. After passage of the required volume of stripping gas, the pumping is stopped and the adsorption filters are extracted.

An appropriate amount of the standard compound is added to the filter prior to extraction. The filter is extracted using four portions of solvent of 50 μl each by passing the solvent up and down the filter five times by means of pressurized nitrogen.

Finally, the extract is transferred into a 1.5-ml sample vial stoppered with a PTFE cap. The recovery is calculated as the ratios of the corresponding relative peak areas in the extract and the reference solution.

Gas chromatography

The GC analyses were performed on a Packard Becker 427 instrument (United Technologies Packard, Delft, The Netherlands). The gas chromatograph was equipped with a home-made splitter provided with a quartz glass liner. The split vent line was provided with a magnetic valve to permit splitless injections. Splitless injection with a low-boiling solvent such as methylene chloride requires an initial oven temperature as low as 25°C. To achieve such a low temperature, the oven was left open during sample transfer into the column. The injector and detector temperatures were usually 250°C, but the detector temperature was sometimes raised to 275°C,
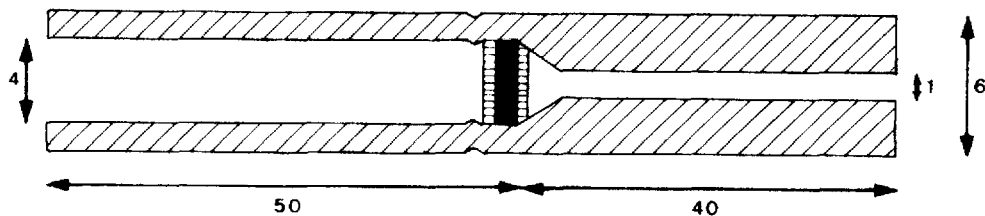

Fig. 2. Adsorption filter tube. Sizes in mm.

depending on the boiling points of the components. Helium was used as a carrier gas. CP-Sil-5 fused-silica columns (Chrompack, Middelburg, The Netherlands) (25 m × 0.25 or 0.32 mm I.D.) were used. The chromatographic data were processed by an SP 4000 data system (Spectra-Physics, Santa Clara, CA, U.S.A.).

THEORETICAL

A theoretical model is derived for the dynamic headspace sampling in order to predict the applicability of the method and the effect of process- and compound-dependent factors on the recovery. The following assumptions are made to permit a mathematical description of the process (see also Fig. 3).

(a) a state of thermodynamical equilibrium exists; at high gas flow-rates, this assumption will not hold; the gas will be under-saturated, resulting in too low experimental recovery values;

(b) the composition of the gaseous phase and the liquid phase is homogeneous; owing to the bubbling of the gas, eventually in combination with stirring, the liquid phase will be homogenized; for the gas phase this will not be valid, which will result in too large experimental recovery values.

(c) the gas flow-rate is constant;

(d) the gas and liquid volumes are constant;

(e) the temperature of the sample is constant;

(f) no breakthrough of the adsorption filter occurs; for stripping gas volumes up to 80 l no significant breakthrough was observed for all compounds investigated.

Starting from the gas–liquid distribution and the mass balance, and some simplifications following from the assumptions above, the trapped amount can be expressed as follows:
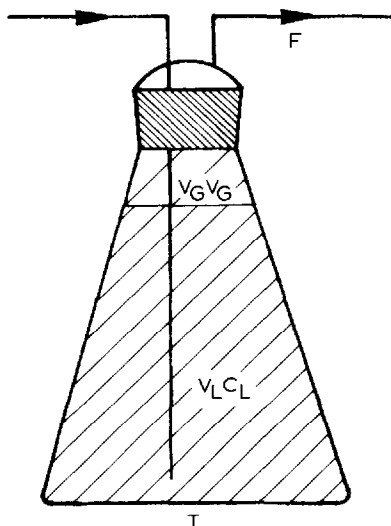

Fig. 3. Schematic representation of the stripping process.

$$m_a = m_0 \left\{ 1 - \exp\left(\frac{-Ft}{KV_1 + V_g} \right) \right\} \qquad (1)$$

where m_a = mass of a component i adsorbed on the filter; m_0 = intial amount of a component i in the sample; F = gas flow-rate; t = process time; V_1 = sample volume; V_g = volume of the gaseous phase; K = mass based gas–liquid distribution constant. This is in full agreement with the equation given by Novak et al.[6], who followed a slightly different derivation. Defining the recovery as the mass ratio of a compound adsorbed on the trap and the initial amount present in the sample, it can be expressed as

$$R = 1 - \exp\left(\frac{-Ft}{KV_1 + V_g} \right) \qquad (2)$$

RESULTS AND DISCUSSION

Influence of component parameters

The dependence of the recovery calculated from eqn. 2 on the volume of the stripping gas is shown in Fig. 4 for different values of $KV_1 + V_g$. Obviously the stripping time will decrease for decreasing values of $KV_1 + V_g$.

The gas–liquid distribution constant is given by

$$K = \frac{V_m}{V_w} \cdot \frac{P_{tot}}{P_i^0 \gamma_i} \qquad (3)$$

where V_w = molar volume of liquid water; V_m = molar gas volume; P_i^0 = vapour pressure of pure i; P_{tot} = total pressure; γ_i = activity coefficient of i in water. For volatile non-polar compounds both γ_i and P_i^0 will be large, resulting in small values
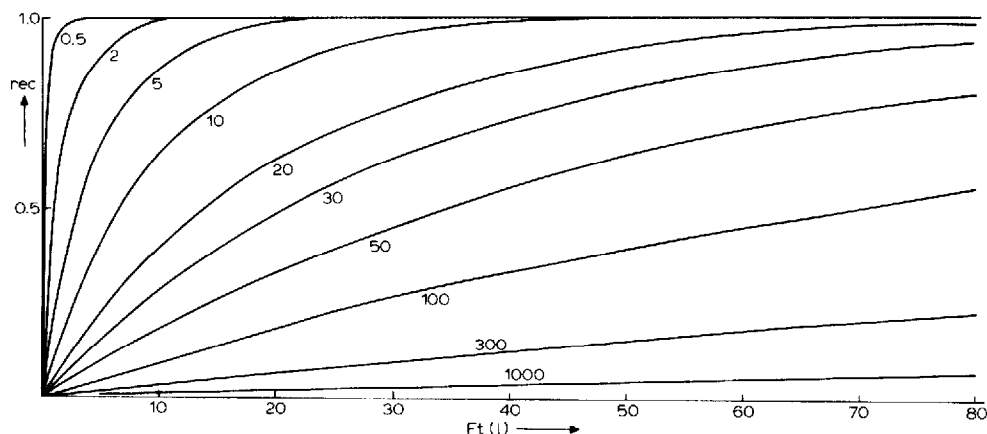

Fig. 4. Theoretical recovery as a function of the stripping gas volume for different values of $KV_1 + V_g$ (0.5–1000 l).

of K. Therefore, KV_1 will be small compared with V_g and the recovery can be approximated by

$$R = 1 - \exp\left(\frac{-Ft}{V_g}\right) \tag{4}$$

This means that for volatile non-polar compounds the recovery becomes independent of vapour pressure and is determined only by the stripping gas volume and the volume of the gaseous phase. With actual values for F (*e.g.*, 330 ml/min) and V_g (*e.g.*, 150 ml) a 99% recovery is achieved after 2 min of processing.

On the other hand, for polar and non volatile compounds, γ_i and P_i^0 will be small and thus K will be large. Now the recovery can be approximated by:

$$R = 1 - \exp\left(\frac{-Ft}{KV_1}\right) \tag{5}$$

Obviously a large stripping gas volume will be required to achieve reasonable recoveries for polar and non-volatile compounds (Ft has to be large in order to counterbalance a large value of K).

Influence of process parameters

From eqn. 2, it follows that a large stripping gas flow-rate, a small volume of the aqueous sample and a small volume of the gaseous phase favour high recoveries. The gas flow-rate is limited by the capacity of the pump and the resistance of tubing and filters. Too large a flow-rate is not advisable. The possible process instabilities that may result will have a negative effect on the stripping efficiency owing to deviations from the thermodynamic equilibria.

To permit the determination of low concentrations, the sample volume should be as large as possible. For polar substances Ft is proportional to V_1, so that large sample volumes would result in long stripping times. For non-polar compounds, however, the stripping time increases less than in proportion to increasing sample volume. This offers the possibility of processing large volumes of water within a reasonable time.

The volume of the gaseous phase is important only when non-polar solutes are treated. There has to be a minimum free space above the water in the sample flask to avoid the penetration of water into the tubing due to splashing.

Extraction of the charcoal adsorption filter

The extraction of the charcoal filter is a very important step in the whole sampling procedure as it has a major influence on the final sensitivity of the method. In order to select the most suitable solvent, the extraction behaviour of five solvents was investigated. Four portions, 50 μl each, of the solvents were used for the extraction of the charcoal filters, which were loaded with an amount of the "multimix" solution corresponding to 200 ng per component. Simultaneously, 200 ng of an internal standard (*n*-octyl chloride) were added.

Approximate extraction efficiencies are presented in Fig. 5 for each of the solvents. With *n*-pentane only paraffinic components are completely desorbed,
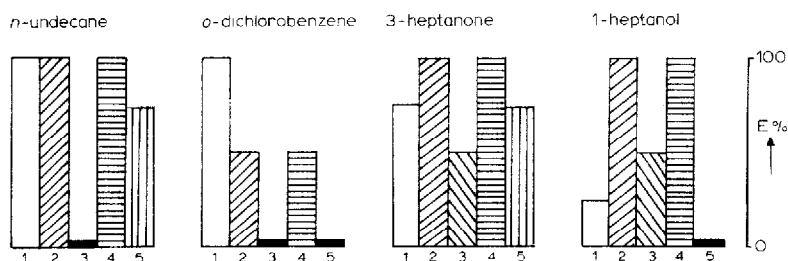
Fig. 5. Schematic representation of the extraction efficiency (E) for four representative components using different solvents: 1 = carbon disulphide; 2 = methylene chloride; 3 = methanol; 4 = ethyl acetate; 5 = n-pentane.

whereas with methanol only alcohols and ketones can be partly extracted. Carbon disulphide cannot be used for the extraction of alcohols and ketones and ethyl acetate is not suitable for extracting aromatics. Methylene chloride appears to be the best choice for most substances, although aromatic compounds will not be extracted completely, as can be seen in Table I. Therefore, methylene chloride was selected as the extraction solvent throughout the investigations. The relative standard deviation of the extraction process is of the order of 3% for loadings ranging from the ppb to the tens of ppt levels, using different 5 mg filters.

Reproducibility and accuracy

With the equipment and the procedure described under Experimental, the overall reproducibility of the dynamic headspace sampling was determined for stripping gas volumes of 10 and 20 l. The concentration of the aqueous "multimix" samples was about 200 ppt for each component. The sample temperature was 25°C.

Average overall recovery values are summarized in Table II. Note that the overall standard deviation includes errors due to the sample preparation, the strip-

TABLE I

EXTRACTION EFFICIENCY (%) FOR DIFFERENT FRACTIONS OF METHYLENE CHLORIDE

Solvent	Fraction No.				
	1	2	3	4	Total
n-Hexyl chloride	78	18	2		98
3-Heptanone	75	18	—		93
p-Chlorotoluene	28	25	18	13	86
1-Heptanol	69	23	6	1	100
1,2,4-Trimethylbenzene	43	28	16	10	98
o-Dichlorobenzene	10	14	14	15	55
n-Octyl chloride*	75	21	3	—	100
2-Nonanone	76	24	3	—	104
n-Undecane	75	22	4	1	103
1-Nonanol	61	26	9		97
Benzylacetone	55	27	9	4	98

* Internal standard.

TABLE II

AVERAGE OVERALL RECOVERY AND RELATIVE STANDARD DEVIATION OF DYNAMIC
HEADSPACE SAMPLING FOR STRIPPING GAS VOLUMES OF 10 AND 20 l ($n = 4$)

Solvent	Overall recovery (%)			
	10 l		20 l	
	Mean	R.S.D. (%)	Mean	R.S.D. (%)
Toluene	93	6.1	106	1.8
n-Octane	88	13	99	1.9
n-Hexyl chloride	99	9.2	107	3.0
3-Heptanone	7	11	13	14
p-Chlorotoluene	80	13	97	3.6
1-Heptanol	0	—	0	—
1,2,4-Trimethylbenzene	85	19	97	5.5
o-Dichlorobenzene	61	16	82	7.9
2-Nonanone	16	15	29	8.5
n-Undecane	88	13	98	5.1
1-Nonanol	1	118	4	31
Benzylacetone	0	—	0	—

ping process, the extraction step and the GC analysis. The reproducibility of the 20-l
stripping volume ($\sigma \approx 6\%$) is slightly better than for the 10-l stripping volume ($\sigma
\approx 13\%$). The reproducibility of GC analysis, the preparation of the sample and the
reference mixtures was found to correspond to a standard deviation of about 4%.

For components (*e.g.*, of the aromatic type) that will be only partly extracted
from the trap the stripping efficiency was corrected for this effect.

Comparison of calculated and experimental data

According to eqns. 2 and 3 the recovery can be calculated when the vapour
pressure and the activity coefficient are known. Unfortunately, few data are available
in the literature. Therefore, approximate values of the saturated vapour pressure were
calculated from the Clausius–Clapeyron equation, using tabulated values of the heat
of vaporization[7] and the boiling point. Approximate activity coefficients of some of
the compounds involved in this study were calculated from their solubility in water,
which was determined from phase diagrams given by Landolt and Börnstein[8]. Ap-
proximate data for activity coefficients and saturated vapour pressures obtained in
this way are presented in Table III. They were used to calculate the corresponding
recoveries. The calculated and experimental data are in good agreement, as can be

TABLE III

CALCULATED VALUES OF ACTIVITY COEFFICIENT (γ_i) AND SATURATED VAPOUR PRES-
SURE (P_i^0) AT 25°C

Solvent	γ_i	P_i^0 (bar)
Toluene	$9.0 \cdot 10^3$	$39 \cdot 10^{-3}$
1-Heptanol	$6.4 \cdot 10^3$	$0.37 \cdot 10^{-3}$
o-Dichlorobenzene	$5.1 \cdot 10^4$	$1.9 \cdot 10^{-3}$

seen in Fig. 6. For small stripping gas volumes too low experimental values are found, probably owing to non-ideal mixing in the gaseous phase.

Effect of the stripping gas volume

According to the theoretical model, the stripping gas volume greatly influences the recovery. This is illustrated in Table IV, where experimental results obtained with "multimix" solutions with a concentration of 200 ppt per component are presented. The temperature of the sample was 25°C and the gas flow-rate was 330 ml/min, which was the maximum pump capacity. In order to avoid contamination of the sample by breakthrough effects of the cleaning filter (*cf.,* 4 in Fig. 1), which has a much larger capacity than the adsorption filter (*cf.,* 2 in Fig. 1), it was extracted regularly. The breakthrough filter (*cf.,* 3 in Fig. 1), placed in series with the adsorption filter, was extracted after each experiment. It was observed that no serious breakthrough problems arise if less than 80 l of the stripping gas have passed the adsorption filter.

The overall recoveries appeared to be independent of concentration within the limits of the experiment (ppb to tens of ppt level). The results presented in Table IV agree fairly well with the model given above. Non-polar substances are efficiently stripped with only small volumes of the stripping gas, whereas compounds of intermediate polarity such as alcohols yield low recoveries even after prolonged stripping. Considering the behaviour of weakly polar compounds such as 3-heptanone and 2-nonanone, apparently the vapour pressure and the activity coefficient play a competitive role during the stripping process. The latter, although less volatile than 3-heptanone, can be extracted (stripped) much more easily from the aqueous sample, owing to its larger activity coefficient; 2-nonanone is less polar; it has a longer aliphatic chain. The higher stripping recovery of 1-nonanol compared with 1-heptanol can be explained in a similar way. From the stripping recoveries of *n*-octane and *n*-undecane no boiling point effect can be observed, as predicted by the theoretical model (*cf.,* eqn. 4).

TABLE IV

EFFECT OF STRIPPING GAS VOLUME ON THE RECOVERY (%)

Concentration about 200 ppt per component.

Solvent	Stripping volume (l)					
	0.3	3	10	20	40	80
Toluene	38	69	93	106	106	—
n-Octane	74	82	88	99	106	111
n-Hexyl chloride	63	87	99	107	107	111
3-Heptanone	0	7	7	13	18	46
p-Chlorotoluene	28	56	80	97	102	108
1-Heptanol	0	0	0	0	2	2
1,2,4-Trimethylbenzene	34	61	85	97	99	103
o-Dichlorobenzene	17	41	61	82	104	105
2-Nonanone	2	9	16	29	60	79
n-Undecane	72	84	88	98	104	104
1-Nonanol	0	2	1	4	15	20
Benzylacetone	0	0	0	0	0	0

TABLE V

STRIPPING RECOVERIES (%) AT DIFFERENT TEMPERATURES AND DIFFERENT STRIP-PING GAS VOLUMES

Sample, "multimix" solution; concentration, about 200 ppt per component.

Solvent	10 l			20 l		
	25°C	35°C	45°C	25°C	35°C	45°C
Toluene	93	103	107	106	—	—
n-Octane	88	93	99	99	—	—
n-Hexyl chloride	99	103	103	107	—	—
3-Heptanone	7	14	26	13	26	45
p-Chlorotoluene	80	101	102	97	99	102
1-Heptanol	0	5	6	0	2	5
1,2,4-Trimethylbenzene	85	101	102	97	99	102
o-Dichlorobenzene	61	—	99	82	99	111
2-Nonanone	16	32	48	29	48	70
n-Undecane	88	101	100	98	99	98
1-Nonanol	1	14	17	4	6	16
Benzylacetone	0	0	0	0	0	0

Effect of the temperature of the sample

The stripping recoveries are expected to improve at higher temperatures owing to the increased vapour pressure. According to the Clausius–Clapeyron equation, a temperature increase of 10°C will result in about double the vapour pressure for compounds with a boiling point between 400 and 600°K and a heat of vaporization varying from 40 to 60 kJ/mol. It follows from the theoretical model (*cf.*, eqn. 5) that a 10°C increase in temperature will have approximately the same effect on the stripping recovery as stripping twice as long.

In Table V, stripping recoveries at different temperatures and for different stripping gas volumes are given. Diluted "multimix" solutions with concentrations of about 200 ppt per component were used throughout this experiment. Comparing the effects of the increase in temperature and of the stripping gas volume (*e.g.*, temperature 25–35°C and stripping gas volume 10–20 l), it can be concluded that the results agree reasonably well with the theory. This is particularly true for components with moderate polarity (*e.g.*, ketones, aromatics), with exception of the alcohols. For less polar compounds the effect is similar but the agreement with the theory is less obvious.

Effect of the boiling point of the solutes

The effect of the vapour pressure on the overall recovery is shown in Fig. 7. For a diluted "hydrocarbon mix" with concentrations of about 200 ppt per component, recoveries of 90% and above were achieved for n-alkanes with up to 13 and 17 carbon atoms with 10 and 40 l of stripping gas, respectively, and a temperature of the sample of 25°C. The limiting boiling point could be only slightly improved by increasing the temperature of the sample to 45°C.
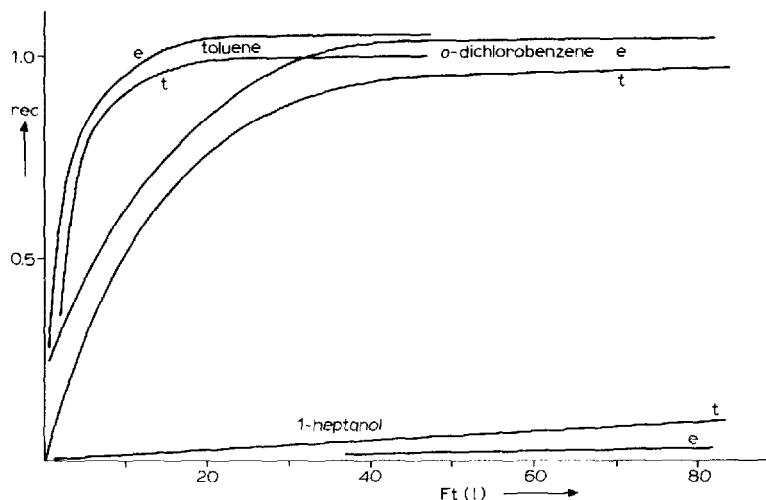
Fig. 6. Comparison of the calculated (t) and experimental (e) recoveries as a function of the stripping gas volume. Concentrations of the components: about 200 ppt per component.

Effect of the polarity of the solutes

Limitations of the stripping process with respect to the interactions between the solutes and the aqueous sample were investigated by processing a "phenolic mix" solution with a concentration of about 200 ppt per component. The stripping gas volume was 40 l and the temperature of the sample was 45°C. None of the components was recovered under these conditions. Equilibrium constants of phenol and o-cresol ($K = 5.6 \cdot 10^{-5}$ and $1.3 \cdot 10^{-4}$ respectively) were calculated from literature data for the given experimental conditions. Substituting these values into the recovery
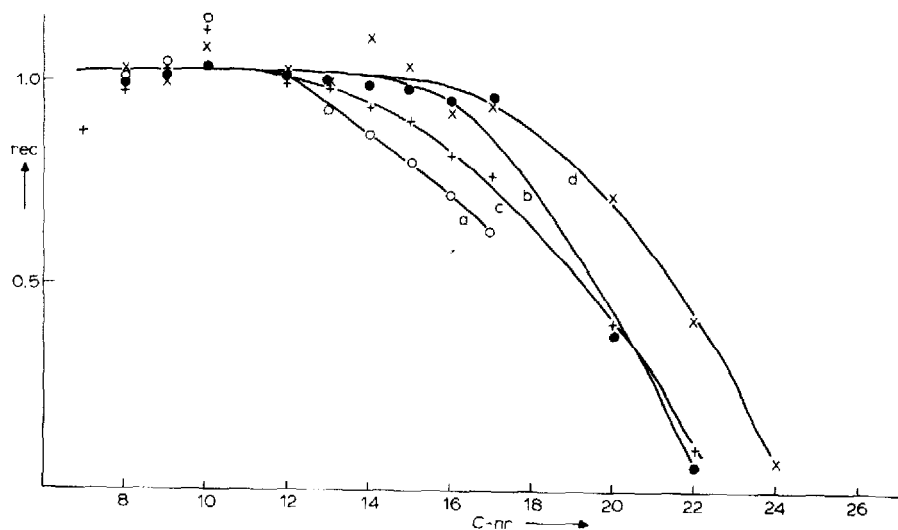

Fig. 7. Effect of an increasing carbon number of n-alkanes on the recovery of stripping for four temperature–stripping gas volume combinations; (a) 25°C–10 l; (b) 25°C–40 l; (c) 45°C–10 l; (d) 45°C–40

equation (eqn. 2), it follows that for a 10% recovery of phenol and o-cresol stripping gas volumes of 1800 and 800 l, respectively, would be required. Obviously, it cannot be expected that phenols can be recovered within a reasonable time using dynamic headspace techniques.

CONCLUSION

Dynamic headspace sampling can be applied to the enrichment of organics in aqueous samples down to very low concentrations (ppt level). It has been shown theoretically and experimentally that the nature of the solute and its volatility and polarity can greatly influence the recovery and the processing time. Methylene chloride appeared to be the most suitable universal extraction solvent. Improved recoveries or shorter process times can be achieved at elevated temperatures.

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