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Equilibrium Sorptive Enrichment on Poly(dimethylsiloxane) Particles for Trace Analysis of Volatile Compounds in Gaseous Samples

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A novel approach for sample enrichment, namely, equilibrium sorptive enrichment (ESE), is presented. A packed bed of sorption (or partitioning) material is used to enrich volatiles from gaseous samples. Normally, air sampling is stopped before breakthrough occurs, but this approach is not very successful for weakly retained compounds (volatiles) as early breakthrough occurs. In ESE, sampling is continued until all compounds of interest are in equilibrium with the sorptive material. This allows accurate sampling of volatiles and enrichment at the maximum attainable sensitivity. However, due to the equilibrium nature of ESE, it is limited to samples with a constant concentration over the sampling time. This requirement is easily met for those compounds with short equilibration times (volatiles). Because of the nature of the sorption mechanism, which is basically dissolution, all compounds partition independently into the sorbent (stationary phase) and displacement effects do not occur. This is a great advantage over adsorption materials. Additionally, theory allows the calculation of enrichment factors from literature retention indexes. Moreover, ESE also benefits from the features of sorption materials such as a very high inertness and interference-free blanks. The performance of ESE is illustrated with the analysis of several analytes including the epoxides ethylene oxide and epichlorohydrin in real-life air sampling.

Most of the techniques presently used for the preconcentration of volatile organic compounds (VOCs) in air and gaseous samples are based on adsorption of the analytes of interest on a suitable preconcentration material followed by either liquid or thermal desorption.[1−3] Commonly used adsorbents include carbon-based materials such as activated carbon and carbon molecular sieves[4,5] and porous organic polymers such as Tenax and Chro-

mosorb.[6] Thermal desorption is increasingly being used as a sensitive alternative to liquid desorption. Here, the trapping material is heated and the analytes released at high temperatures (typically 200−300 °C) are transported to the analytical column by the carrier gas. Thermal desorption allows the rapid and complete transfer of the entire sample to the GC column, resulting in maximum sensitivity. Therefore, the performance of thermal desorption procedures is in many cases superior to liquid desorption. Unfortunately, thermal desorption embraces some typical problems. Where in liquid desorption, blank levels are almost solely determined by the purity of the solvent, in thermal desorption, blanks are caused by the adsorbent itself. At the high temperatures used, adsorbents tend to break down (especially polymeric ones), resulting in characteristic degradation peaks.[7] Additionally, at elevated temperatures during thermal desorption, the adsorbent might react with the analytes to form artifacts[8,9] as was recently observed for sulfur compounds[10] or might permanently bond them to the surface. These are of course highly undesirable effects. Moreover, the unpredictable nature of adsorbents (batch-to-batch variation and the dependence of the retaining power on sample humidity and sample concentration) renders the reliable application of adsorption even more difficult.

The performance of traps packed with poly(dimethylsiloxane) (PDMS) as an alternative to adsorbents was recently evaluated.[11] PDMS is very inert, as is well known from gas chromatography. Permanent adsorption and reactions on PDMS are negligible. The performance of PDMS for the enrichment of a number of analytes was compared to that of the adsorbents Chromosorb, Carbotrap, and Tenax. For many polar (and/or reactive) compounds, much better performance in terms of recoveries was observed on PDMS. A marked disadvantage of PDMS, however, is the low capacity for volatile compounds; e.g., *n*-heptane has a breakthrough volume of less than 250 mL on 300 mg of PDMS at room temperature. This not only results in diminished sensitivity compared to sampling on adsorbents but also renders sampling difficult. First,

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timing a short sampling period can be difficult also with respect to start-up effects. Second, temperature becomes a very important factor as it has an exponential influence on the breakthrough volume.

In this contribution, a novel approach for PDMS sample enrichment is proposed. Whereas sampling is normally stopped when the first compound starts to be lost from the trap (break-through sampling), sampling is stopped when all analytes are in equilibrium with the PDMS sorbent. This approach is referred to as equilibrium sorptive enrichment (ESE). Equilibrium sampling of air was already carried out by several authors using, e.g., SPME,[12] but in this contribution a packed bed is applied as an equilibrium sampling device. Compared to SPME, it has the advantage that it contains a significantly larger quantity of PDMS (typically 500 times more) resulting in a proportional sensitivity increase and that flow control through a packed bed is much better than that of "free" flow around an SPME fiber. Equilibrium techniques are well suited for the determination of analyte concentrations over short sampling periods (up to 10 min) such that the sample input concentration can be assumed to be constant. Longer sampling times (e.g., daily or weekly averages) cannot be applied due to fluctuations in input concentration. In ESE, analyte enrichment factors are no longer dependent on the sample volume but solely on the partitioning equilibrium constant (K), sample pressure, and temperature. These dependencies will be described in the Theoretical Section. ESE also benefits from the typical features of PDMS sorption such as high inertness and fast desorption and relies on the predictability of equilibrium constants. Several applications illustrate the use of ESE for the enrichment of volatile and unstable compounds from gaseous samples.

THEORETICAL SECTION

Calculation of Enrichment Factors. In ESE, the gaseous sample is sampled until the compounds of interest are in equilibrium with the sorbent. Sampling is thus stopped (far) beyond the breakthrough point for (most) compounds. This also means that calibration cannot be performed with a simple liquid calibration solution as described previously for breakthrough sampling.[11] Instead, a continuous stream of calibration gas coming from a gas cylinder or a headspace device is necessary. One of the advantages of PDMS sorption is that it was already extensively studied in the past because PDMS is the most commonly applied GC stationary phase. Literature data on the retention of many compounds are available as Kovats retention indexes.[13] In a previous publication,[14] a simple approach was presented to calculate equilibrium constants (K) from retention indexes (RI). In the equilibrium sorption mode, the gas phase is in full equilibrium with the PDMS sorbent and the sorbed volume of air is equivalent to the retention volume of the trap. The concentration of a compound in the gas phase, C (in kg/m³) can be calculated by

$$C = \frac{m_{\text{sorbed}}}{V_{\text{r}}} = \frac{m_{\text{sorbed}}}{V_0(1 + K/\beta)} \approx \frac{m_{\text{sorbed}}}{V_{\text{PDMS}}K} \quad \text{for} \quad K \gg 1 \tag{1}$$

in which m_{sorbed} is the sorbed amount of the compound under

investigation (in kg), V_{r} is the retention volume of the trap (in m³), V_0 is the dead volume of the trap (in m³), V_{PDMS} is the volume of PDMS (in m³) in the trap, and β is the phase ratio. For practical purposes, the approximation can be used. V_{PDMS} is determined by weighing the amount of PDMS present and conversion with its density of 825 kg/m³. K is calculated from retention indexes, and m_{sorbed} is determined from a calibration curve.

Influence of Pressure Drop. Calculation of the equilibrium sorbed amount of a compound using eq 1 is only valid when the concentration of the sampled gas is constant over the length of the trap. At low flow rates, this requirement is often met, but when the sampling flow rate is set too high this is no longer the case. As a consequence of the sorption mechanism, at lower sampling pressures (where the gas-phase concentration, expressed as kg/m³ is lower), the amount of analyte partitioning into the sorbent (m_{sorbed}) will be proportionally lower. The pressure profile inside the trap has therefore to be known from which an average pressure over the trap length can be calculated. The packed bed can be either under turbulent or laminar flow conditions, but most often it will be in an intermediate flow regime. The parameter expressing the degree of turbulence is the Reynolds number (Re):

$$Re = \rho v_0 d_{\text{p}}/\mu \tag{2}$$

where ρ is the gas-phase density (in kg/m³), v_0 the superficial velocity (in m/s), d_{p} the particle diameter (in m), and μ the viscosity (in kg/ms). Under normal conditions, i.e., sampling with a vacuum pump), the gas pressure will decrease through the bed whereas the superficial velocity will increase. Since μ and d_{p} are independent of pressure and ρv_0 is a constant throughout the bed, Re is a constant through the bed and thus the degree of turbulence is also constant. It can be noted that whereas in an open tubular column the transition from laminar to turbulent flow is abrupt at a Re of ~2300, in a packed bed this transition is much more gradual with a fully laminar flow at $Re < 1$ and a fully turbulent flow at $Re > 1000$. The practical working range for air enrichment traps is $Re\ 1-100$. The actual pressure drop over a small piece of packed bed is given by[15]

$$\frac{\partial p}{\partial x} = \frac{150\mu v_0}{d_{\text{p}}^2}\frac{(1 - \epsilon)^2}{\epsilon^3} + \frac{1.75Gv_0}{d_{\text{p}}}\frac{1 - \epsilon}{\epsilon^3} \tag{3}$$

where p is the pressure in the bed (in kg/ms²), x the length coordinate through the bed (in m), G the mass flow through the section of the bed (equal to ρv_0, in kg/(m² s)), and ϵ the porosity. The first part of eq 3 describes the behavior of the packed bed under laminar flow conditions whereas the latter part describes the turbulent flow regime. Since all parameters in eq 3 are independent over the bed except v_0, eq 3 can be reduced to

$$\partial p/\partial x = Av_0 \tag{4}$$

where A is a constant. Since v_0 is inversely proportional with p,

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eq 4 leads to

$$\int p\, \partial p = \int A'\, \partial x \qquad (5)$$

where A' is another constant. Equation 5 can be integrated to lead to the average pressure over the bed:

$$f = \frac{2}{3}\frac{P^3 - 1}{P^2 - 1}P_{in} \qquad \text{with} \qquad P = \frac{P_{in}}{P_{out}} \qquad (6)$$

where P_{in} and P_{out} are the trap inlet and outlet pressures. The true equilibrium sorbed amount of a compound is now given by $m_{sorbed}*f/P_{in}$, where m_{sorbed} is the amount of compound partitioned into the PDMS phase without pressure drop effects.

EXPERIMENTAL SECTION

Thermal Desorption Cartridges. Prepacked (cross-linked) PDMS traps were obtained from Gerstel (Müllheim a/d Ruhr, Germany) and conditioned for 1 h at 300 °C and then for 4 h at 250 °C. After this procedure, no peaks appeared in the blank chromatogram with the exception of cyclic siloxanes. PDMS tubes have an inner diameter of 4 mm and are packed with PDMS particles in the range 250−500 μm.

Experimental Setup. The experimental setup used was described previously.[11] In short, it consists of a TDS-2 thermodesorption unit (Gerstel) mounted on a HP6980/5973 GC/MSD system (Hewlett-Packard, Little Falls, DE) also equipped with a flame ionization detector (FID). Desorption was carried out under a helium flow of 150 mL/min. A CIS-4 PTV injector (Hewlett-Packard) is used for cyrofocusing the analytes prior to transfer onto the analytical column. Two analytical columns were used, a 30 m $L \times 320$ μm i.d. $\times$ 4 μm d_f CP-SIL5CB column (Chrompack, Middelburg, The Netherlands) and a 30 m $L \times 320$ μm i.d. $\times$ 10 μm d_f Porabond Q (Chrompack). The GC was programmed from 35 °C (4 min) at 15 °C/min to 275 °C. The temperature during sampling was kept at 22.5 $\pm$ 0.1 °C.

Chemical Standards. The BTX gas mixture was obtained from BOC specialty gases (Guildford, Surrey, U.K.). This sample contained benzene, toluene, and p-xylene (BTX) at a concentration of 25 ppm in helium. Other gaseous samples were generated in situ in a homemade headspace device previously described.[16] A small amount of liquid, present in a vial, is placed inside a small glass bulb. A continuous nitrogen stream is supplied which causes a steady evaporation of the liquid forming a stable (spiked) concentration in the outgoing nitrogen stream. By measuring the flow rate of the gas used and the weight loss of the vial, the outgoing concentration can be calculated.

RESULTS AND DISCUSSION

Prediction of Enrichment Factor. Using the 25 ppm BTX standard gas mixture, the accuracy of the enriched concentration, predicted by eq 1, was investigated. A stream of 1 L of nitrogen (grade 5.0) per minute was supplied to the homemade headspace device. To this, a flow from the BTX cylinder was added to generate a final concentration of 0.1 ppm. To double-check the
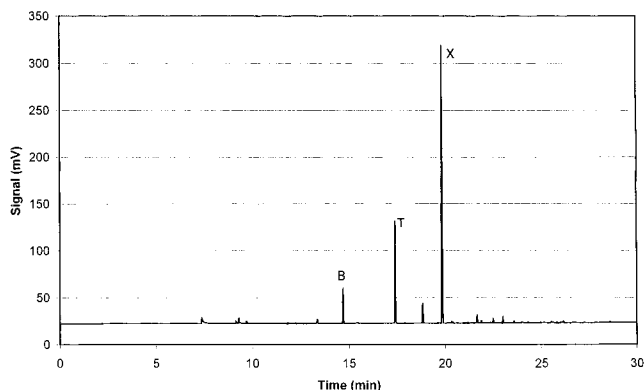
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Figure 1. Chromatogram of the enrichment of a 0.1 ppm mixture containing benzene (B), toluene (T), and p-xylene (X) on a tube containing 0.45 mL PDMS. Sample volume, 6 L; sampling flow rate, 0.1 L/min. Temperature during sampling, 22.5 $\pm$ 0.1 °C. Column, 30 m $L \times$ 320 μm i.d. $\times$ 4 μm d_f CP-SIL5CB. Detection, FID.

Table 1. Enrichment of the BTX Mixture on a Trap Containing 0.45 mL of PDMS Phase[a]

component	RI[13]	K[14]	m_{sorbed} (ng)	C (ppb)	detctn limit (ppb)
benzene	654.13	419	17.2	91	0.5
toluene	756.49	1106	40.9	82	0.2
p-xylene	857.45	2891	125	96	0.08

[a] Listed are literature data on retention indexes (RI) from which K values were determined on the PDMS trap. The detected amount of each component (m_{sorbed}) was calculated using a liquid calibration solution spiked on the PDMS trap. Detection limits are specified for a signal-to-noise ratio of 8. Values listed are the average over three experiments.

accuracy of this spiking level, in a separate series of experiments, a vial filled with benzene was placed in the headspace device to which now clean air is supplied. Over a certain period (24 h), the weight loss of this vial can be observed, and together with the air flow rate, the spiking level was easily found. In this way, the accuracy of the 0.1 ppm dilution out of the gas cylinder could be confirmed. From this gas stream, 6 L was sampled through a PDMS tube containing 0.45 mL of material at a flow rate of 100 mL/min to ensure full equilibration between the PDMS phase and the gas sample without pressure drop effects. A chromatogram from an enriched BTX sample is shown in Figure 1 and illustrates the principle of ESE quite effectively. Though in the original sample all compounds were present in equal concentration, in ESE, compounds with increasing partitioning constant (e.g., p-xylene) are enriched to a larger extent than compounds with lower partitioning constants (e.g., benzene).

From this chromatogram, absolute detected amounts were determined using a calibration line constructed from several direct injections of a liquid calibration solution onto the PDMS material. Absolute detected amounts (m_{sorbed}) are listed in Table 1 as well as the corresponding concentrations calculated using eq 1. The determined concentrations are somewhat smaller than the 0.1 ppm level from the reference gas. Apparently, compounds seem to partition slightly less into the PDMS particles than predicted by eq 1. This can have numerous causes of which the most obvious are erroneous literature RI data or a slightly higher temperature during sampling. This deviation is acceptable for practical work,
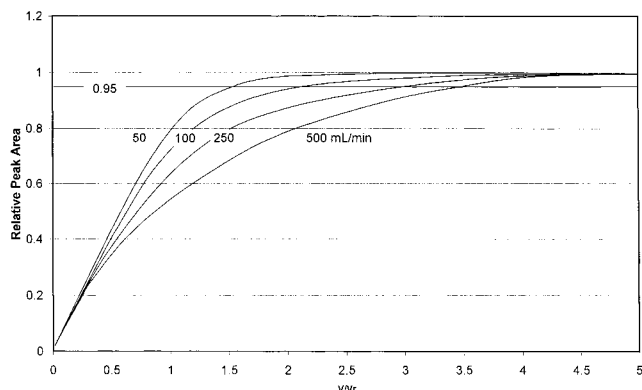
Figure 2. Enrichment of an air sample spiked with five alkanes (*n*-pentane though *n*-nonane). Different volumes were sampled at a flow rate of 50 mL/min. Peak areas are expressed relative to the peak areas obtained for infinite sampling time, and sampling volume is expressed relative to a compound's retention volume. Data are based on a 0.45-mL PDMS trap.
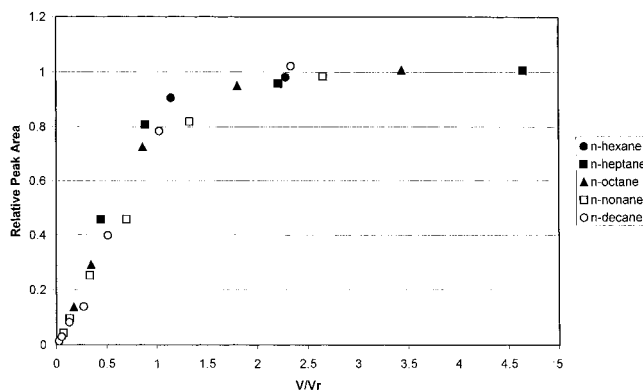

Figure 3. Sorption profiles of *n*-hexane on a 0.45-mL PDMS trap at room temperature (22.5 °C). Sampling flow rate was varied between 50 and 500 mL/min.

Table 2. ESE of a Gas Sample Spiked with *n*-Hexane at 2 ppm and Different Concentrations of Acetone[a]

acetone concn (ppm)	peak area of *n*-hexane	displacement [b] (%)
0	488	0
5	489	0
50	488	0
500	486	0.4
5000	461	5

[a] Each entry is the average of four sequential experiments, RSD = 3.6%. Flow rate during sampling was 50 mL/min. PDMS trap of 0.45 mL.

especially since the reproducibility of the ESE analyses was very good at an average RSD of 5% ($n = 3$) for the test analytes. Detection limits for BTX with FID detection are listed in the last column of Table 1 for a signal-to-noise level of 8. Detection limits are sub-ppb for all compounds and are, due to the nature of ESE, lowest for *p*-xylene, which has the highest partitioning constant. In real-life samples, detection limits can be higher because of the presence of chemical interferences. Lower detection limits can be achieved by using either a more sensitive (and/or selective) detector like the mass spectrometer in the ion monitoring mode or lower trapping temperatures.

Equilibrium Sorption Profile. The nature of the ESE sorption profile was investigated in the following way. A solution containing 1% of five alkanes, namely, *n*-pentane through *n*-nonane, was prepared in methanol. A 5-mL sample of this solution was placed in a 10-mL vial inside the homemade headspace device, and a continuous flow of 0.5 L/min clean air (grade 4.5) was introduced. From the outlet of the headspace device, gas was sampled at a flow of 50 mL/min using a constant-flow sampler (Gillian Instrument Corp., West Caldwell, NJ) avoiding in this way pressure drop effects (due to the low sampling flow rate applied). Sampling times from 1 to 90 min were used to follow the saturation of the 0.45 mL of PDMS phase. The temperature was 22.5 °C during these experiments. Results of the analyses are summarized in Figure 2. Peak areas were normalized to the peak areas found (or suspected) at infinite sampling time. The sample volume (V) was divided by the retention volume (V_r) to obtain the relative sample volume. In this way, similar sorption profiles are obtained for all compounds.

In the sorption profiles, two interesting parts can be distinguished. The part of the curve for which $V/V_r < 0.5$ is linear and represents "normal" breakthrough sampling. Here, peak area is directly proportional to the sampled volume. The part of the curve for which $V/V_r > 2$ represents the equilibrium enrichment region where the sorbed amount of compound is no longer dependent on the sampled volume. For (V/V_r) values in excess of 5 (not shown in Figure 2), relative standard deviations become very small, as will be shown later. This is of course ideal for quantitative sampling. However, in cases where sampling times need to be minimized, it is acceptable to sample only until V/V_r equals 2.

Additionally, the required (minimum) equilibrium sampling volume depends on the flow rate at which sampling is performed. This is illustrated in Figure 3 where sorption profiles for *n*-hexane on 0.45 mL of PDMS are shown at flow rates between 50 and 500 mL/min. At higher flow rates, a larger volume has to be sampled to reach equilibrium. At a flow rate of 50 mL/min, V/V_r is roughly 1.6 at 95% of the equilibrium whereas at a flow rate of 500 mL/min this point is only reached at a V/V_r of 3.4. A doubled sample volume at a 10 times increased flow rate, however, still implies a reduction in sampling time by a factor of 5. Therefore, high flow rates are in general to be preferred as long as pressure drop effects do not occur.

Displacement Effects. One of the most important advantages of enrichment by sorption is the absence of displacement effects. Normally when adsorbent phases are employed, a compound present in a very high concentration tends to push others off from the active sites of the surface of the adsorbent. In ESE, the equilibrium mechanism, in principle, allows independent partitioning of all solutes. This was investigated by using a gas stream spiked with a constant concentration of *n*-hexane. Additionally, a certain amount of acetone was added and the amount of *n*-hexane sorbed was followed. The results of these experiments are listed in Table 2. Displacement only occurs at acetone concentrations of ∼5000 ppm, which are very unrealistic to occur in practice. Consequently displacement can be assumed to be negligible.

High-Flow Sampling. Influence of Pressure Drop. The influence of a pressure gradient through a PDMS sorption cartridge under ESE conditions was investigated in the Theoretical Section. Using eq 6 it can be concluded that the maximum theoretical analyte loss due to a pressure drop is 33%, which is

Table 3. Influence of a Pressure Drop on the Enrichment of *n*-Hexane Spiked at 2 ppm in Air[a]

flow (mL/min)	P_{in} (mbar)	P_{out} (mbar)	f/P_{in} (theor)	peak area of hexane	recovery
50	1024	1015	0.995	332	1
150	1024	988	0.983	329	0.988
300	1024	912	0.946	306	0.922
620	1024	839	0.912	289	0.870
1000	1024	755	0.856	265	0.798
1250	1024	603	0.798	237	0.713
1450	1024	524	0.770	231	0.696

[a] PDMS trap of 0.45 mL.

too much to ignore. Using again the 2 ppm *n*-hexane standard in air, the influence of pressure drop was investigated. Using different flow rates, different pressure drops were generated and the amount of *n*-hexane on the PDMS trap was determined. In- and outlet pressures were measured using digital pressure gauges (Gerstel) which were calibrated to an accuracy of 1 mbar. The results are listed in Table 3. Both the theoretical *f* factor from eq 6, which is calculated solely on the basis of the in- and outlet pressures, and the experimentally determined recovery relative to the situation without pressure drop are given in Table 3. The experimentally determined pressure drop loss is slightly higher than that calculated from theory. This error can have several causes including inaccurate pressure measurements (not likely as the instrumentation used was recently calibrated), slight temperature deviations, or slight concentration variations from the headspace device. A 5% loss in analyte occurs at a flow rate of ∼200 mL/min and a 10% loss at ∼500 mL/min. In most cases, a 10% loss is still acceptable. Therefore, it is recommended to work at flow rates below 500 mL/min, but if this results in unacceptably long sampling times, higher flow rates can be used, however only with the use of a correction for the pressure drop.

ESE Determination of Epichlorohydrin. After the theoretical studies, some challenging compounds in air were sampled by ESE to illustrate its performance and the inertness and favorable characteristics of PDMS. Epichlorohydrin, a not too volatile solute (RI = 696.3), is not easily enriched on classical adsorption materials because of destruction and reactions of the epoxide ring. On a PDMS trap of 0.45 mL, epichlorohydrin has an equilibrium volume of 280 mL as calculated from the equations described by Baltussen et al.[14] Therefore, 1000 mL of air was sampled at 100 mL/min to guarantee equilibrium under absence of a pressure drop. Analyses were accomplished on the GC-MSD system using selective ion monitoring (SIM) in the positive chemical ionization (PCI) mode with methane as reagent gas. The latter was selected for enhanced selectivity since PCI allows quantification on the MH$^+$ ion, which is more specific than the lower m/z fragment ions generated under EI conditions. Figure 4 shows the chromatogram for the selected ions at m/z 93, 65, and 63 obtained from the enrichment of an air sample containing 0.2 ppb epichlorohydrin. A 56-pg sample epichlorohydrin was thus collected on the PDMS trap. Epichlorohydrin is clearly detected without interferences; detection limits are around 10 ppt.

MONITORING ETHYLENE OXIDE IN AIR

Ethylene oxide (EO) is another important air contaminant difficult to monitor at trace levels in work places. It is a highly
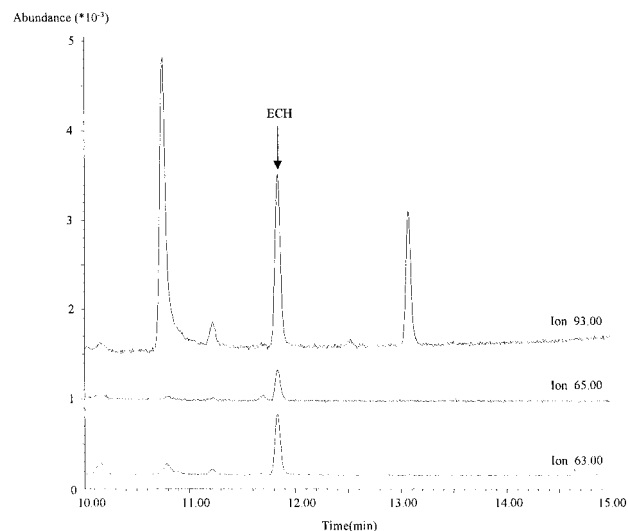

Figure 4. ESE enrichment of epichlorohydrin spiked at 0.2 ppb in air. Column, 30 m L × 320 μm i.d. × 4 μm d_f CP-SIL5CB. Detection, MSD operated in the PCI−SIM mode.
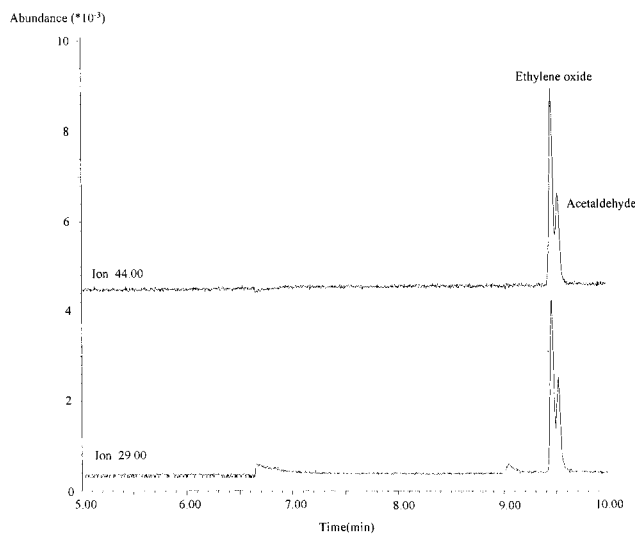

Figure 5. ESE enrichment of EO from a spiked air sample (0.5 ppm). First peak is EO, second peak is acetaldehyde. Detection, MSD operated in the EI-SCAN mode. Specific ions were extracted from the total ion current. Column, 30 m L × 320 μm i.d. × 10 μm d_f Porabond Q.

volatile (RI = 424.4) and unstable compound. Enrichment of EO from air samples is normally done using HBr-impregnated silica cartridges to convert the analyte into 2-bromoethanol. This compound is subsequently eluted from the cartridge with acetone and an aliquot is injected into a GC-ECD instrument. Disadvantages of this approach include a reduced sensitivity (only an aliquot is injected) and many manual handling steps. For enrichment by ESE, an equilibrium sorption volume of 15 mL was calculated from the retention index for EO. During 10 min, air spiked at the 0.5 ppm level was sampled at a flow rate of 50 mL/min to ensure complete equilibrium of a PDMS trap containing 0.45 mL of material. Figure 5 shows the chromatogram obtained on the Porabond Q column. Detection was done on the MSD in the electron impact (EI)-SCAN mode, scanning from 10 to 200 amu. Ions 29 and 44 were extracted from the total ion current. EO is clearly identified; however, one interference was present corre-

sponding to acetaldehyde. Both compounds generate the same mass spectrum and thus cannot selectively be detected with MS. Detection limits are ~20 ppb, but in real-life samples this level may not be reached if large quantities of acetaldehyde are present. Lower detectability can be reached on a more selective column in combination with SIM detection.

CONCLUSIONS

Equilibrium sorptive enrichment is a valuable extension on the volatile side of the PDMS working range. It can be applied for the sampling and quantification of volatiles over short sampling periods. It has been shown that displacement effects are absent due to the sorption mechanism of the PDMS phase so that highly reliable sampling is guaranteed. The equilibrium nature of the sampling process ensures a high reproducibility of typically 5% RSD. For quantitation purposes, enrichment factors can be calculated from literature retention indexes and gaseous standards are not required for routine analysis. Enrichment of volatile and reactive compounds is possible without degradation losses because of the high inertness of the PDMS sorbent. Recommended flow rates are below 500 mL/min to avoid pressure drop effects, and V/V_r should be at least 2.