

# Mixed Sorbent Phases for Thick Film Open Tubular Traps

Jonas Bonn, Johan Redeby, and Johan Roeraade\*

Royal Institute of Technology, Dept. of Analytical Chemistry, SE- 100 44 Stockholm, Sweden

## Abstract

In this work, we present a technique for the preparation of tailor-made sorbent phases for thick film open tubular traps. Solid or liquid polymers are dispersed in a polydimethylsiloxane (PDMS) pre-polymer, which is cross-linked in situ after coating. The technique is evaluated by preparing thick film open tubular traps with PDMS containing solid or liquid poly(ethylene glycol) (PEG). A significant increase in retention for polar analytes is observed, even when only 7.5% PEG is present. The increase in retention for 3-chloro-1,2-propanediol is more than tenfold. The preparation method is simple and no solvents are required. Also, the concept provides great flexibility in terms of phase composition.

## Introduction

Trace and ultra-trace analysis is of central importance in many application fields, such as environmental monitoring of volatile organic compounds (1), flavor analysis in food (2), or analysis of volatile organic compounds in drinking water (3). Sample enrichment is usually required and this is often performed by solid-phase extraction, whereby the analytes of interest are adsorbed onto the surface of a material with a very high surface-to-volume ratio (4). The most common method to release the adsorbed substances is by means of thermal desorption, which has the advantage that no solvents are required. However, due to the high temperatures required, problems may arise like degradation of analytes (5) and/or artifact formation (6).

An alternative to adsorbent-based enrichment emerged about two decades ago with the introduction of polydimethylsiloxane (PDMS) wall-coated capillary traps (7). Here, the analytes are sorbed (dissolved) into the bulk of the trapping material, rather than adsorbed onto its surface. Later, open tubular traps (OTT) with thicker films and thus higher enrichment capacity were developed (8) followed by a number of techniques such as solid-phase microextraction (SPME) (9), stir bar sorptive extraction (SBSE) (10), gum phase extraction (GPE) (11), and high capacity sorptive extraction (12). The relatively weak dispersive interactions between analyte and sorbent generally leads to lower

distribution constants than obtained with adsorbents. On the other hand, lower desorption temperatures can be employed, thus reducing the problems with degradation and artifact formation. Other benefits of sorption are a higher degree of inertness and lack of displacement effects (13).

Although sorbent-based enrichment techniques have grown tremendously in popularity, there are still only a limited number of sorbent phases available. For high capacity extraction techniques such as SBSE (10) and thick film OTT (14,15), where large sorbent volumes are used, only PDMS has been employed. However, being non-polar, PDMS has a rather limited retention power for polar volatiles, and for this type of analytes, the use of alternative enrichment phases would therefore be desirable.

When using thick films of sorbent enrichment phases, it is important that these materials show a high diffusivity towards the analytes, enabling a fast mass transport during sample collection and thermal desorption. PDMS is one of the most permeable polymers available (16), which is a major reason why this polymer has been favored in high extraction capacity systems. For these techniques, the diffusive length in the enrichment phase is often 100  $\mu\text{m}$  or more.

In this paper, a new technique for the preparation of tailor-made sorbent phases is presented. The rather straightforward procedure is based on physically dispersing a liquid or solid material, non-miscible with PDMS, into a PDMS-prepolymer. After curing the PDMS-prepolymer, the dispersed material effectively becomes immobilized and possible phase separation is therefore counteracted. The technique was evaluated using OTT, coated with a thick film of PDMS, containing finely dispersed, non-crosslinked liquid or solid polyethylene glycol.

## Materials and Methods

### Chemicals

PDMS (Sylgard 184, base and curing agent, Dow Corning, MI) was obtained from Sikema, Sweden. PEG-600 [average molecular weight: 600, glass transition temperature ( $T_G$ ), 20–22°C] and PEG-20k ( $T_G$  60–65°C) were purchased from Sigma-Aldrich (St. Louis, MO) and Merck (Darmstadt, Germany), respectively. Hexane, isopropanol, 1,2-ethanediol [CAS#107-21-1], 1,3-dichloro-2-propanol (1,3-DCP) [CAS#96-

\* Author to whom correspondence should be addressed.

23-1], 3-chloro-1,2-propanediol (3-MCPD) [CAS#96-24-2], and methanol were of *pro analysi* quality and purchased from Sigma-Aldrich.

### Preparation of the OTT

Glass tubes (0.7-mm i.d. and 1.5-mm o.d.) were used for preparing the traps. The tubes were coiled in-house, resulting in a coil diameter of ~ 16 cm. Circa 10 cm of each end of the coil was left straight to facilitate the connection of fused-silica capillary transfer lines (inner diameter 320  $\mu\text{m}$ ). Three traps were manufactured; one with 7.5% (w/w) PEG-600 (liquid at room temperature) in PDMS, one with 7.5 % PEG-20k (finely mixed and dispersed), and finally one with 7.2% PEG-20k particles (particle size between 36–71  $\mu\text{m}$ ). Dynamic coating of the tubes was performed as previously described (17). Briefly, the glass tube was placed in a gas chromatography oven (room temperature) and filled with the dispersed PEG/PDMS prepolymer from a pressurized vessel. Additional pressurization of the tube blew out the bulk of the material, leaving behind a thick film on the wall of the tube. The film of prepolymer coating was polymerized by quickly raising the temperature of the GC oven, while maintaining a gas flow through the tube. This resulted in an average film thickness of ~ 100  $\mu\text{m}$ .

The first two traps were manufactured by mixing the PEG with PDMS, using a combination of manual stirring, machine mixing using a DI 25 Basic homogenizer (IKA Werke GmbH & Co, Germany) and finally by sonication with a Sonics VCX 750 ultrasonic processor (Sonics and Materials, CT). This resulted in very small (sub-micrometer) particles of homogeneously dispersed PEG. After stirring the curing agent into the dispersion according to the instructions of the PDMS manufacturer, the mixture was set to de-aerate in a vacuum desiccator. Removal of air from the mixture was necessary in order to avoid bubble formation during curing of the coating inside the capillary. The trap containing the coarse PEG particles was made in a slightly different manner. These particles were prepared by grinding large commercial PEG-20k flakes under liquid nitrogen, using a mortar and pestle. The ground flakes were fractioned using two sieves, pore size 71  $\mu\text{m}$  and then 36  $\mu\text{m}$  (Fritsch GmbH, Germany). The sieved flakes and curing agent were manually stirred into the PDMS prepolymer. As the capillary tube was

filled, the mixture was stirred with a magnetic stirrer, to prevent settling of the particles in the filling reservoir. All traps were cured at 150°C under a flow of nitrogen for 15 min and thereafter conditioned at 200°C for 1.5 h, while maintaining the flow of nitrogen. Average film thicknesses were determined by means of gravimetric measurements. As a reference trap, an OTT containing pure PDMS was used. This trap had previously been prepared according to a dynamic coating procedure with an instant thermal film fixation (18) resulting in a smooth film. The properties of the different traps are listed in Table I.

### Scanning electron microscopy

Micrographs of the morphology of the different polymer mixtures were obtained using a LEO 1530 FEG scanning electron microscopy (SEM) (Carl Zeiss SMT AGNTS GmbH, Oberkochen, Germany). Samples were prepared by tearing pieces of the polymerized materials apart, in order to obtain a clean, smooth surface from the bulk of the material. The samples were covered with a sputtered Au/Pd layer prior to SEM analysis.

### Evaluation of distribution constants and efficiency

Distribution constants ( $K_c$ ) for a number of components, as well as plate heights ( $H$ ) for isopropanol vs. average flow rates were determined for the traps and compared to the values, obtained with the reference PDMS trap. The GC used was a 6890 GC (Agilent Technologies, Palo Alto, CA), equipped with a split injector and two detectors [flame ionization detector (FID) and thermal conductivity detector (TCD)]. The traps were connected to the GC via short pieces of deactivated fused silica tubing (ca. 30 cm long, 320  $\mu\text{m}$  i.d., Agilent Technologies, #160-2325) using connectors and polyimide/carbon ferrules (ZU1 and ZF1V, VICI AG, Switzerland). The oven temperature was kept at 25°C, and nitrogen was used as carrier gas. 1  $\mu\text{L}$  injections (split ratio 5:1) were made using an autoinjector (G1513A, Agilent Technologies). Carrier gas flow rates were determined by means of a soap bubble meter.

### Determination of water uptake

The following procedure was used to determine the amount of water retained when sampling from environmental air in equilibrium mode. The trap was placed inside a GC oven set to 25°C. In the sampling mode, one end of the trap was connected to a Minipuls 3 peristaltic pump (Gilson, WI) via an air-actuated six-port valve (A4C6UWE, VICI AG, Switzerland) while the other end of the trap was connected to the air to be sampled, also via the valve. A schematic of the setup is shown in Figure 1. The GC injector was connected to the TCD via the switching valve using two pieces of deactivated fused-silica capillary tubing (each 20 cm long, i.d. 320  $\mu\text{m}$ , Agilent). The air temperature and the relative humidity were determined using a combined humidity meter and thermometer (Therm 2285-2 B Alhborn, Germany). During sampling, ambient air was sucked through the trap at 10 mL/min by the peristaltic pump. To establish equilibrium conditions for water vapor in the trap, the sample volume was set to three times the estimated breakthrough volume of water. After sampling was completed, the six-port valve was switched to desorption mode. In this mode, the carrier gas was routed through the trap in backflush

**Table I. Properties of the Prepared Traps**

|   | Trap # 1 | Trap # 2 | Trap # 3                       | Trap # 4                         |
|---|----------|----------|--------------------------------|----------------------------------|
| PEG content [%]                                     | 0        | 7.5      | 7.5                            | 7.2                              |
| Average molecular weight of PEG [g/mol]             | –        | 600      | 20000                          | 20000                            |
| Physical state of PEG                               | –        | liquid   | particles (< 1 $\mu\text{m}$ ) | particles (36–71 $\mu\text{m}$ ) |
| Trap length [cm]                                    | 155      | 200      | 284                            | 200                              |
| Trap I.D. [mm]                                      | 0.718    | 0.718    | 0.713                          | 0.713                            |
| Sorbent volume [ml]                                 | 0.28     | 0.34     | 0.55                           | 0.30                             |
| Average film thickness [ $\mu\text{m}$ ]            | 91.0     | 84.3     | 101.7                          | 75.2                             |
| Phase ratio ( $\beta$ ), void volume/sorbent volume | 1.26     | 1.41     | 1.04                           | 1.65                             |

direction, into the TCD. Nitrogen was used as the carrier gas (10 mL/min), and the desorption was performed at 35°C. Calibration of the TCD was performed by splitless injection of pure water, with the injector temperature maintained at 100°C and the valve positioned in the desorption mode.

### Determination of the diffusion constant of isopropanol

Van Deemter curves for isopropanol on a PDMS capillary column (DB-1, L: 30 m, i.d.: 0.32 mm,  $d_f$ : 5  $\mu$ m, Agilent Technologies) and a cross-linked PEG capillary column (DB-Wax, L: 30 m, i.d.: 0.25 mm,  $d_f$ : 0.25  $\mu$ m, Agilent Technologies). Column were plotted for average linear velocities between 8 and 123 cm/s (7 points). The GC parameters were as follows: oven temperature, 25°C; inlet temperature, 200°C; split ratio, 100:1; FID temperature, 250°C. Hydrogen was used as carrier gas. The retention time of methane was used to measure the dead volume.

## Results and Discussion

One of the reasons for using PDMS in high capacity sorption systems is its high diffusivity towards analytes, even after cross linking (16). Cross-linking is necessary because this ensures mechanical stability and durability of the sorbent phase. Other cross-linked materials, such as phenyl- or cyanopropyl-substituted polysiloxanes or PEG have not been used, most likely because of their poor diffusivity. This would lead to an increase in the time necessary for analytes to diffuse into and out of the sorbent, resulting in impractically long sampling and desorption times. In this study, we aimed for an increased polarity of the sorbent phase, while maintaining the favorable high diffusivity properties of PDMS. The strategy was to incorporate a certain percentage of PEG in the PDMS. Mixed phases have been used in chromatographic capillary columns, but only thin films have been prepared, by statically coating a glass capillary from a dilute solution (19). In the case of very thick films, this procedure cannot be utilized. Moreover, the conventional solution-based

static coating procedure is only applicable if the stationary phases can be dissolved in one and the same solvent.

The concept of physically mixing the undiluted polymers, as proposed in this paper, provides a great degree of freedom in the choice and relative proportions of the mixed polymers. The only requirements are that the polymers do not react with each other and retain their chemical integrity at the elevated temperatures applied during the desorption process.

Literature data regarding the diffusivity of PEG are scarce; therefore a short study was performed in which Van Deemter curves for isopropanol, using PDMS as well as cross-linked PEG capillary columns were obtained. These curves should reflect the extended Golay equation, as reported by Giddings et al. (20):

$$H = \frac{2D_m^0 \times j \times f}{\bar{u}} + \frac{r^2 (1 + 6k + 11k^2) \times f \times \bar{u}}{24D_m^0 (1 + k)^2 \times j} + \frac{2k \times d_f^2 \times \bar{u}}{3(1 + k)^2 \times D_s} \quad \text{Eq. 1}$$

Where  $D_m^0$  and  $D_s$  are the diffusivity in the gas phase at the outlet pressure and in the stationary phase, respectively,  $j$  is the James-Martin gas compressibility factor,  $f$  is the Giddings' plate height correction factor,  $r$  is the column radius,  $\bar{u}$  is the average mobile phase linear velocity,  $d_f$  is the stationary phase film thickness, and  $k$  is the retention factor. Fitting Equation 1 to the obtained data resulted in  $D_s$ -values for isopropanol in PDMS and cross-linked PEG of  $6.0 \times 10^{-6}$  cm<sup>2</sup>/s and  $1.9 \times 10^{-7}$  cm<sup>2</sup>/s, respectively. Thus, the diffusion constant for isopropanol in cross-linked PEG is less than 1/30th than that in PDMS. It is, therefore, evident that cross linked PEG is not very suitable for thick-films of sorbent phase.

A benefit of the mixed-phase preparation method, reported in this paper, is that it is possible to incorporate non cross-linked polymers, because the bulk cross-linked PDMS phase will act as a mechanical support matrix. A non cross-linked PEG should show a somewhat higher diffusivity than a cross-linked PEG, particularly when using small molecular weight material. In fact, the method of physically entrapping PEG in cross-linked PDMS allowed the preparation of a trap, containing small droplets of liquid PEG-600.

### Evaluation of the mixed phases using SEM micrography

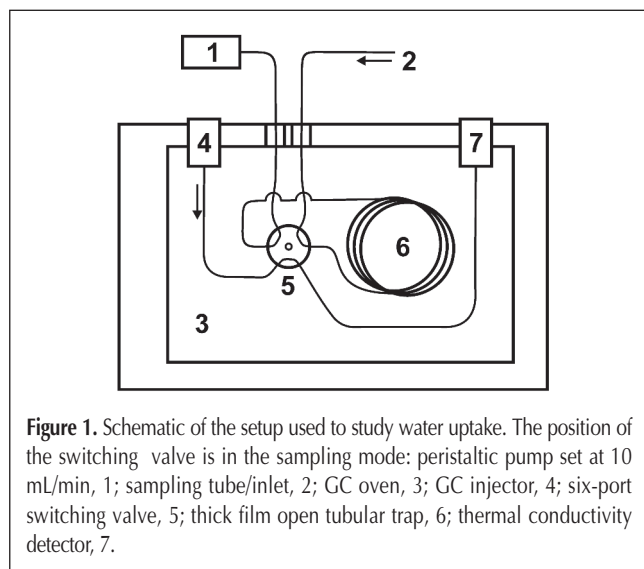
In order to visually evaluate the dispersion of the PEG in PDMS, SEM images of the cross-linked mixed phase were made. Figure 2 shows such an image of 7.5% PEG-600 in cross-linked PDMS, where the presence of micrometer-sized entities in the bulk PDMS can be observed.

Crater-like structures can be noted across the surface of the material, along with some black holes, which we believe are air bubbles in the PDMS. The craters are probably imprints left by PEG particles, which either were removed upon ripping of the polymer, or were mechanically scraped off the surface during preparation for the SEM. Some craters contain PEG particles, as seen in the lower image in Figure 2.

The upper part of Figure 3 shows the finely dispersed, sub-micron particles of PEG-20k, whereas the lower image shows the coarser, sieved particles embedded in PDMS.

### Distribution constants and efficiency of the traps

Evaluation of the new sorbent phases was carried out with two





issues in mind: the selectivity and diffusivity towards polar analytes of the sorbent phase. Elution analysis of pure compounds with nitrogen gas was performed to investigate the retention behavior of the new phases. Table II lists the experimentally obtained distribution constants for three of the traps.

It can be concluded that a significant increase of retention for the polar compounds is obtained by the addition of only 7–8% of PEG to the PDMS phase. The most pronounced increase was achieved for the highly polar diols, which seems logical. For 3-MCPD, which is a toxic trace compound present in food products made from acid-hydrolyzed vegetable protein, such as soy sauce (21), the increase is more than one order of magnitude. Another conclusion was that  $K_c$  of (the non polar) hexane is more or less unaffected by the addition of PEG.

To determine the degree of resistance to mass transfer, elution analysis using the three traps listed in Table II was performed. The plate height at different flow rates was determined using isopropanol as analyte. The results obtained are shown in Figure 4. Because the sampling rate, and not separation time is of primary interest, the following discussion will be based on the actual flow rates through the traps rather than gas velocities.

In the OTT technique, a low plate number

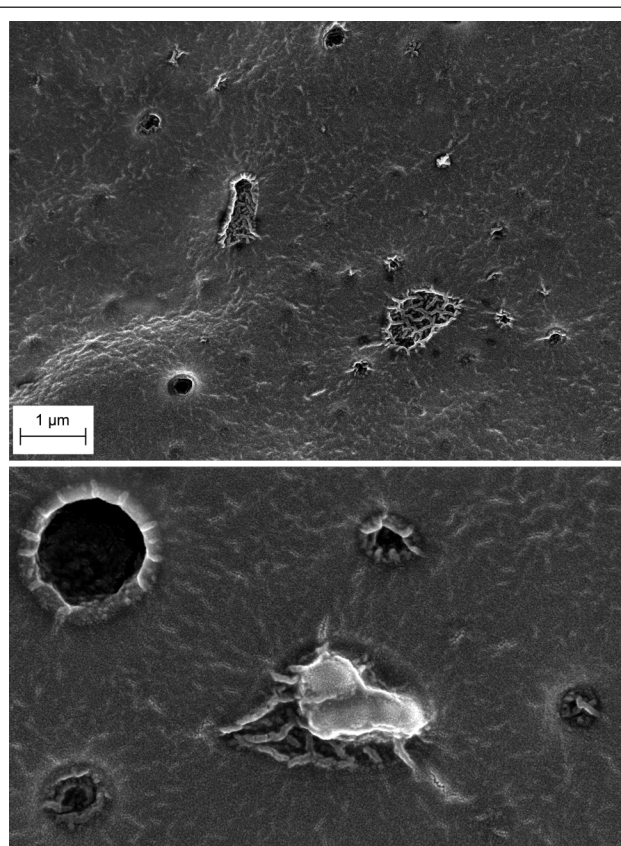
leads to a reduced breakthrough volume (22). Therefore, it was of interest to measure the efficiency of the different traps. As can be seen in Figure 4, the plate height of the polar isopropanol is only slightly increased with the addition of liquid or solid PEG. The polarity of the sorbent phase has thus been increased without any significant loss in efficiency of the trap. This was a very positive finding but the reason for this may not be immediately evident. The explanation is that the plate height is influenced by the retention factor according to Equation 1. Due to the

**Table II. Distribution Constants (Including 95% Confidence Intervals) Determined for Three Different Phases and for a Number of Compounds\***

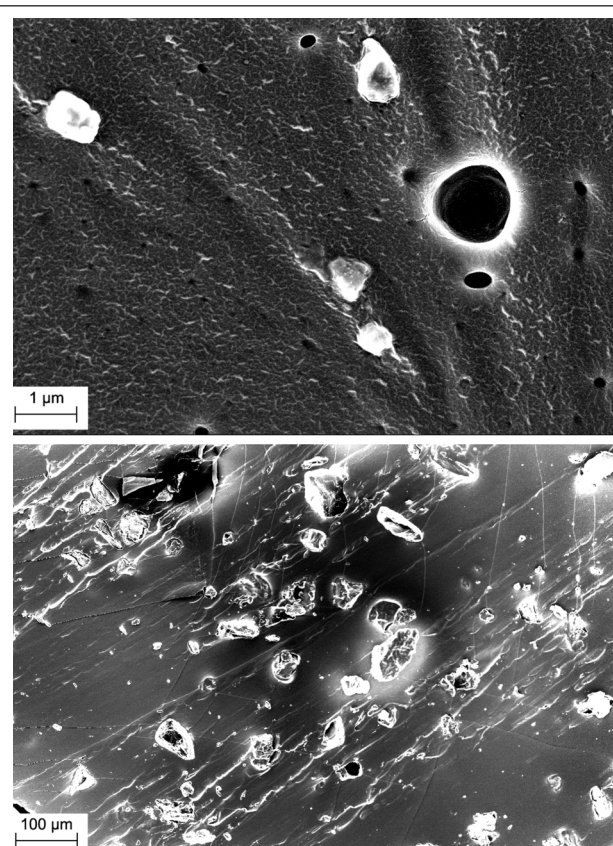
|                            | CAS#     | Measured distribution constants |                                      |  |
|----------------------------|----------|---------------------------------|--------------------------------------|--|
|                            |          | Trap #1<br>100 % PDMS           | Trap #2<br>PDMS with<br>7.5% PEG-600 | Trap #3<br>PDMS with 7.5%<br>PEG-20k (< 1 $\mu$ m) |
| Methanol                   | 67-56-1  | 45 $\pm$ 1                      | 114 $\pm$ 3                          | 87 $\pm$ 4   |
| Hexane                     | 110-54-3 | 204 $\pm$ 3                     | 211 $\pm$ 4                          | 204 $\pm$ 4  |
| <i>n</i> -Propanol         | 71-23-8  | 227 $\pm$ 7                     | 490 $\pm$ 11                         | 344 $\pm$ 17                                       |
| Isopropanol                | 67-63-0  | 123 $\pm$ 2                     | 202 $\pm$ 4                          | 210 $\pm$ 4  |
| 1,3-DCP <sup>†</sup>       | 96-23-1  | 1050 $\pm$ 34                   | 3340 $\pm$ 168                       | 2194 $\pm$ 107                                     |
| 1,2-Ethandiol <sup>†</sup> | 110-80-5 | 527 $\pm$ 24                    | 2810 $\pm$ 141                       | 4235 $\pm$ 207                                     |
| 3-MCPD <sup>†</sup>        | 96-24-2  | 2524 $\pm$ 117                  | 30900 $\pm$ 1552                     | 29790 $\pm$ 1455                                   |

\* These values were determined through elution analysis at a temperature of 25°C.

<sup>†</sup> The distribution constant was determined at 50°C to reduce the elution volumes.



**Figure 2.** SEM micrographs of cross-linked PDMS, containing submicron-droplets of PEG-600 (7.5%). The upper image shows craters at 10000 times magnification. The lower image shows a PEG particle in the crater.



**Figure 3.** The upper image shows finely divided ultrasonicated PEG-20k, embedded in cross-linked PDMS. The lower image shows sieved 36–71  $\mu$ m PEG-20 k particles, embedded in cross-linked PDMS.

very thick films present in the traps, the third term in Equation 1 completely dominates the contribution to  $H$ .  $H$  is proportional to  $d_f$  squared and approximately inversely proportional to  $k$ . The differences in  $d_f$  between the PEG-containing traps and the 100% PDMS reference trap are rather small (trap #2:  $\sim +7\%$  and trap #3:  $\sim -12\%$ , Table I), whereas the differences in the retention factors are significantly larger. The calculated  $k$ -values ( $k = K_c/\beta$ ) of isopropanol for the 100% PDMS trap is 98, whereas the value is 143 (+46%) for trap #2, and 202 (+107%) for trap #3. Thus, for a polar compound, such as isopropanol, the negative effect on it, caused by the decrease in sorbent diffusivity introduced by the PEG is effectively counteracted by the increased retention factor.

In the next stage, we investigated the diffusivity properties of the three phases. As already mentioned, the third term in Equation 1 completely dominates the contribution to  $H$ . Simplifying accordingly and rewriting the Golay-equation using flow rate rather than linear gas velocity leads to the following expression (23):

$$H = \frac{2}{3\pi \times D_s} \times \frac{K_c}{(K_c + \beta)^2} (\sqrt{1 + \beta} - \sqrt{\beta})^2 \times F \quad \text{Eq. 2}$$

Where  $F$  is the average flow rate and  $\beta$  is the ratio between the void volume and the sorbent volume of the trap. The equation is valid for the small pressure drops in our OTTs, and for  $K_c$ -values between 50 and 300, provided that  $K_c \gg \beta$  (23). Rearranging Equation 2 and approximating the ratio  $K_c/(K_c + \beta)^2$  with  $1/K_c$  (since  $K_c \gg \beta$ ) gives:

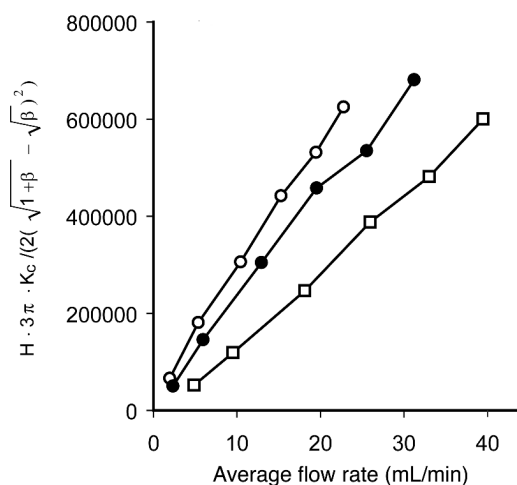
$$\frac{H \times 3\pi \times K_c}{2 \times (\sqrt{1 + \beta} - \sqrt{\beta})^2} = \frac{F}{D_s} \quad \text{Eq. 3}$$

Plotting the left term of Equation 3 against the average flow rate results in graphs, where the slopes are the reciprocal of  $D_s$  of the phases (Figure 5). It should be pointed out that the traps,

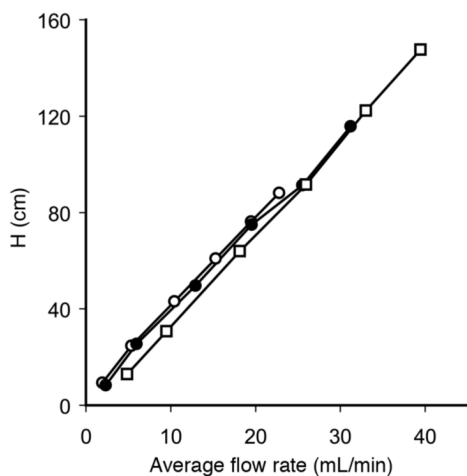
coated with the mixed phases, have irregular films, which has been shown to increase the plate height by roughly 30% (17).

Apparently, the presence of non cross-linked PEG in the sorbent phase lowers the diffusivity to some extent. Regression analysis of the curves in Figure 5 revealed that the diffusion constant for isopropanol in the PDMS was  $1.1 \cdot 10^{-6} \text{ cm}^2/\text{s}$ , whereas  $D_s$  was 40% and 26% lower for the sorbent in trap #2 and trap #3, respectively. The sub- $\mu\text{m}$  PEG 20-k particle-containing phase shows somewhat higher  $D_s$  than the PEG-600 phase. The reason for this outcome is not entirely clear at the moment.

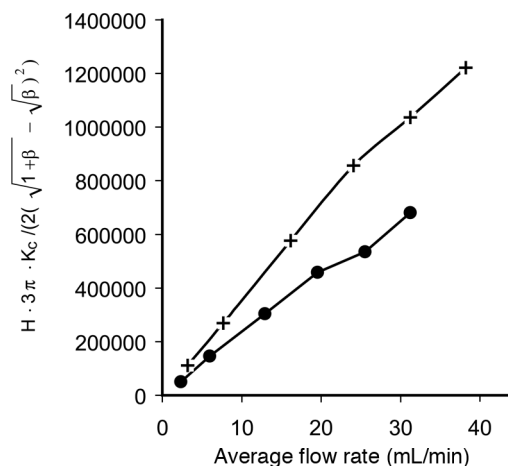
To reveal the influence of the size of the PEG particles on the efficiency of the traps, similar plots as shown in Figure 5 were



**Figure 5.** The left term of Equation 3 vs. average flow rate for PDMS and PEG-containing traps.  $\circ$  = PEG-600 (trap #2);  $\bullet$  = PEG-20k sub- $\mu\text{m}$  particles (trap #3);  $\square$  = 100% PDMS (trap #1).



**Figure 4.** Plot of  $H$  vs. flow rate for isopropanol from two PDMS-traps containing PEG and one 100% PDMS trap.  $\circ$  = PEG-600 (trap #2);  $\bullet$  = PEG-20k sub- $\mu\text{m}$  particles (trap #3);  $\square$  = 100% PDMS (trap #1). NB: these plate heights are fully acceptable for sampling purposes, as only a few plates are required for effective trapping (22).



**Figure 6.** Plot of the left term of Equation 3 vs. average flow rate for traps with different sized PEG-20k particles.  $\bullet$  = sub- $\mu\text{m}$  particles (trap #3);  $+$  = 36–71  $\mu\text{m}$  particles (trap #4).

created for the two traps containing PEG-20k (sub- $\mu\text{m}$  and 36–71  $\mu\text{m}$  particles, respectively) (Figure 6).

Studying the data obtained from the two traps, one can observe that the use of larger (36–71  $\mu\text{m}$ ) PEG particles resulted in larger plate heights than for the case where sub- $\mu\text{m}$  particles were utilized. This is according to expectation; the longer diffusion lengths in the larger PEG particles should cause an increase in resistance to mass transfer.

### Water uptake

Increasing the polarity of a sorbent, as compared to pure PDMS, will invariably lead to an increase in water uptake if the sample contains water. In applications where a subsequent gas chromatographic separation is performed, the water uptake can become a limiting factor. If large amounts of water enter the GC separation system, problems will be experienced, such as chromatographic peak splitting (24) or ice plug formation in a setup employing cryofocusing. The amount of trapped water is basically determined by the sample volume and the humidity of the sample. When very large sample volumes are passed through a trap, the water in the gas sample will be in equilibrium with the entire sorbent. For this case, one can calculate the maximum amount of sorbent ( $V_{\text{phase}}$ ) that can be utilized, by defining a tolerable amount of water trapped ( $n_{\text{water}}$ ) and the maximum relative humidity of the gas sample ( $\text{RH}_{\text{max}}$ ). The maximum allowable volume of sorbent phase will be equal to the tolerable amount of water divided by the water concentration in the sorbent phase. This concentration is in turn equal to the water concentration in the sampled air ( $c_{\text{water, air}}$ ) multiplied with the distribution constant. Thus:

$$V_{\text{phase}} = \frac{n_{\text{water, tolerable}}}{K_c \times c_{\text{water, air}}} \quad \text{Eq 4}$$

Using the ideal gas law, the concentration of water in the gaseous sample can be described as:

$$c_{\text{water, air}} = \frac{P_{\text{sat}} \times \text{RH}_{\text{max}}}{R \times T} \quad \text{Eq 5}$$

where  $P_{\text{sat}}$  is the saturated vapor pressure of water at the temperature  $T$ , and  $R$  is the universal gas constant.

Combining equations 4 and 5 gives:

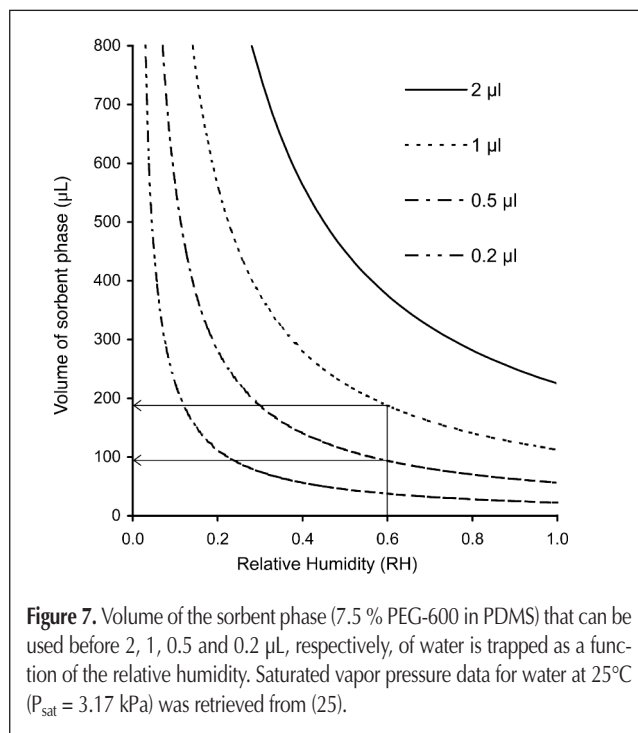
$$V_{\text{phase}} = \frac{n_{\text{water, tolerable}} \times R \times T}{K_c \times P_{\text{sat}} \times \text{RH}_{\text{max}}} \quad \text{Eq 6}$$

In Figure 7, this relationship is shown for the phase consisting of 7.5% PEG-600 in PDMS. For this phase,  $K_c$  for water was determined to be 386 by means of elution analysis. The four traces in the figure represent different amounts of water trapped. The tolerable amount of water will, of course, depend on the chromatographic system used, but 0.5–1  $\mu\text{L}$  can in many cases be considered to be a maximum. This amount of water and a RH of 0.6 (for example) allow the use of between 94 and 189  $\mu\text{L}$  of this sorption phase, as indicated by the arrows in Figure 7, which would contain as much as 7–14  $\mu\text{L}$  of pure PEG-600 phase.

The practical usefulness of Equation 6 was tested by comparing a theoretical calculation with the experimental data. The trap used was the same as that employed in Figure 7. The water uptake of this trap in equilibrium sampling at 22°C and 27% relative humidity was determined to be 0.80  $\mu\text{L}$ . Using Equation 6 in a rearranged form, a  $K_c$  value of 386, and  $P_{\text{sat}}$  (22°C) equal to 2.64 kPa (25), a theoretical value of 0.68  $\mu\text{L}$  retained water is obtained. This is in rather good agreement with the experimental value and a confirmation that the PEG modified PDMS traps have limited use in a high humidity sampling atmosphere due to the PEG affinity to water.

### Conclusions

The procedure described in this paper allows a fast and simple production of stable and highly permeable polymer mixtures. Tuning of the selectivity can easily be accomplished by varying the relative amount and type of phases that are mixed together. The concept has been evaluated using mixtures of PEG and PDMS, but other phases such as siloxanes substituted with cyanopropyl, phenyl, or trifluoropropanol groups should be straightforward. The water uptake from moisture-containing matrices must be taken into consideration when selecting the type and amount of sorbent phase mixtures. An interesting future application would be sampling of nitro-containing analytes, such as various explosives, using a mixed phase containing poly(trifluoropropylsiloxane), which has a unique selectivity for nitro groups (16). The use of our mixed phase concept should also be straightforward in sampling techniques such as SPME, SBSE, or GPE. Applications using the presented mixed-phase concept will be reported in a subsequent paper.



**Figure 7.** Volume of the sorbent phase (7.5% PEG-600 in PDMS) that can be used before 2, 1, 0.5 and 0.2  $\mu\text{L}$ , respectively, of water is trapped as a function of the relative humidity. Saturated vapor pressure data for water at 25°C ( $P_{\text{sat}} = 3.17 \text{ kPa}$ ) was retrieved from (25).



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