

Thick film traps with an irregular film Preparation and evaluation

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Abstract

A new method for preparation of sorbent-based ultra-thick film traps for concentration of trace volatile components from gaseous matrices is described. The procedure is based on blowing a prepolymer (polydimethylsiloxane) through a capillary tube, forming an irregular film of stationary phase. Subsequently, the prepolymer is immobilized in a few seconds by heating to 200 °C. Evaluation of the performance of the new traps showed that the loss of efficiency, compared to regular smooth film traps is only on the order of 20–30%. In terms of breakthrough volume, this loss in performance is rather insignificant. The technology is extremely simple and allows a rapid and cheap production of a large number of ultra-thick film traps, even in non-specialized laboratories. The method can be applied to any type of cross-linkable stationary phase, thereby expanding the scope of sorbent-based trapping and preconcentration concept. Many applications are anticipated in trace and ultra-trace analysis in a wide range of fields, such as environmental chemistry, polymers, food and process analysis.

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1. Introduction

Despite great progress in sampling methodology and column technology, quantitative determination of trace amounts of volatile organic compounds is still somewhat of a challenge. At the same time, there is an increased demand for reliable determination of trace volatiles in fields such as polymers, food, environmental chemistry and advanced materials. For analysis at ppb concentration levels or lower, an analyte enrichment step is usually mandatory.

A vast number of methods for concentration of volatiles have been described [1]. Purge and trap techniques, where the volatiles are collected on a suitable adsorbent are among the most frequently utilized. Direct on-column cryotrapping at very low temperature (liquid N₂) is basically another attractive approach, since it leads to a quantitative enrichment of the analytes. However, the sample volume which can be

handled by this method is normally quite limited due to the presence of water vapour, leading to column blockage by ice plugs. Also, the sampling flow rates which can be applied are very small. For determination of ultra-low concentrations of volatiles, this method is therefore not suitable. However, cryotrapping is extremely powerful for band focusing of water-free analytes (concentrates) onto the head of a capillary column.

Trapping on adsorbents like Tenax-GC, charcoal, etc. is an efficient enrichment strategy, since these materials have a strong affinity for organic compounds, while water is only weakly retained. On the other hand, the strong adsorption makes it more difficult to desorb the volatiles. In a case of thermal desorption, high temperatures may be needed, which may lead to a thermal and/or catalytic decomposition of sensitive target components. Solvent extraction is a milder way for desorption, but, apart from being more complicated, incomplete recovery of the analytes is frequently experienced, as well as losses of volatiles during the solvent removal stage.

During the last decade, there has been an increased trend to utilize sorbents instead of adsorbents. This principle

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utilizes the mechanism of gas/liquid or liquid/liquid partitioning of analytes between the sample and the sorbent, where the sorbent is more or less identical to commonly employed GC stationary phases, usually polydimethylsiloxane (PDMS). The most widespread technologies, based on this principle are solid-phase microextraction (SPME) [2], stir bar sorptive extraction (SBSE) [3], and packed sorptive tubes [4]. In the context of ultra-trace analysis, the SPME technique is not so suitable, due to the very limited amount of stationary phase present. Moreover, this method is based on the establishment of an equilibrium or partial equilibrium with the surrounding gas phase. This complicates quantitative analysis in terms of the calibration protocols, which must be worked out. This is also true for the SBSE technique.

In earlier work, we have described a different concept, where open tubular traps (OTTs), coated with an extremely thick film of cross-linked stationary phase were utilized [5,6]. The method is particularly attractive when operated in the “breakthrough” mode, since inherent quantitative results are obtained in this way. The technique has been utilized in many areas, including pheromones [7], plants [8], environmental air [6,9], wine [10], and preparative GC [11]. Basically, the OTTs have the format of short, wide-bore capillary columns. Solute retention on such traps is determined by partitioning constants, in a similar way as in regular GLC. Due to the extremely low phase ratio of the traps, the retention of solutes can be a 100-fold stronger than on ordinary GC columns, while favourable characteristics such as low pressure drop, and a critical minimum number of theoretical plates are maintained.

To prepare a uniform coating of a very thick layer of liquid phase is not straightforward due to inherent film instabilities. Initially, we solved this problem by an instant cross-linking procedure [5]. However, this coating method is technically demanding, which led others to develop alternative methods. Successful OTTs were prepared by Burger et al. [12], by manipulating a stretched and frozen (liquid N₂) rubber tube into a supporting polyimide-coated fused silica capillary tube. Another strategy was employed by Ortner and Rohwer [13], who utilized a manifold of rubber tubes in order to increase the breakthrough volume of the trap. However, it is difficult to apply these methods for preparation of longer traps, and the choice of stationary phase is restricted to the availability of suitable tubing, which, as far as we know, is limited to silicone rubber only.

In this paper, the preparation of a new type of open tubular trap with a very thick film is described. In contrast to the smooth, regular coatings of conventional OTTs, the new traps are characterized by an irregular film of cross-linked stationary phase. We have investigated the performance data of the traps, and compared their efficiency and breakthrough capacity with data obtained from a regular OTT with a uniform coating. The proposed preparation method is very simple and does not require any expensive or complicated tools. In principle, the technology could be utilized with any type of thermally cross-linkable stationary phase.

2. Experimental

2.1. Preparation of irregular thick film traps

All coating experiments were carried out with the polydimethylsiloxane prepolymer Sylgard 184 (Dow Corning, USA), which is a viscous fluid (5500 mPa s). After thorough mixing of the prepolymer (1–2 ml) with the cross-linking agent according to the instructions of the manufacturer, the mixture was de-aerated under vacuum (20 Torr; 1 Torr = 133.322 Pa) for 30 min.

Initially, wide-bore borosilicate glass capillaries (1.5 mm o.d. × 0.72 mm i.d.) were utilized for preparation of the irregular thick film traps (ITFTs). This facilitated an optimization of the procedure by allowing a visual inspection of the resulting polymer film. The final traps were made of Silcosteel tubing (0.03 in. i.d., Restek, USA; 1 in. = 2.54 cm) since this material, apart from being inert, is far more practical to handle. Prior to the coating procedure, all columns had been coiled (coil diameter of 10 cm), with the two ends (about 7 cm in length each) left straight to facilitate their mounting in the coating device and in instruments used during the subsequent measurements.

A schematic diagram of the coating device is shown in Fig. 1. One end of the capillary was introduced into a glass vial (1.5 ml), via an adapter (Fig. 2), its tip close to the bottom. The vial was filled with the de-gassed prepolymer to ca. three-fourths of its volume and the outlet of the fused silica capillary (0.53 mm i.d.), supplying pressurized nitrogen into the vial, was placed just above the meniscus of the prepolymer.

During the first stage of the coating procedure, the capillary was completely filled with the prepolymer fluid. Subsequently, the vial with the remaining prepolymer was depressurized and replaced with a clean, empty one, while the entrance tip of the filled capillary was wiped off with a lint-free tissue, to remove any prepolymer, adhering to the outside of the tube. The set-up was then placed in the GC oven, and the nitrogen pressure was re-applied to blow the

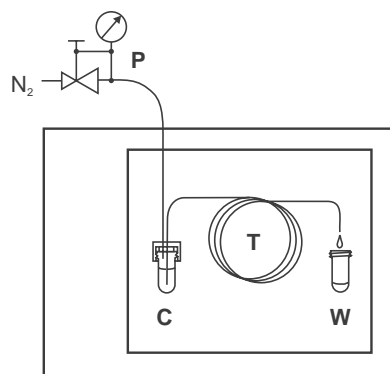


Fig. 1. An illustration of the set-up used for preparation of an ITFT. A standard GC oven was used for polymer cross-linking. P = Pressure regulator; C = coating vial (see Fig. 2); T = capillary trap; W = receiving container for excess prepolymer.

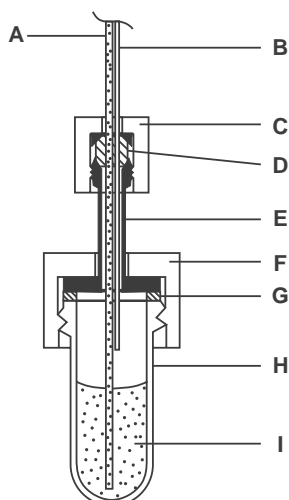


Fig. 2. A schematic drawing of the coating container used. A = Capillary trap; B = fused silica tubing used to pressurize the container with nitrogen; C = Swagelok nut (1/8 in.); D = silicone rubber seal; E = Swagelok union (1/8 in.); F = Schott GL14 nut; G = silicone O-ring; H = 1.5 ml glass vial; I = prepolymer.

bulk of the prepolymer out of the tube. This resulted in the formation of an irregular film of prepolymer on the inner wall of the capillary. In order to immobilize this film, the temperature of the oven was ballistically raised to 200 °C. At this temperature, film fixation occurs within a few seconds. The polymer was further cured for 15 min under the flow of nitrogen.

The average thickness of the coating is dependent on the nitrogen pressure employed to push out the excess prepolymer. In our tests, pressures between 20 and 200 psi were used (1 psi = 6894.76 Pa). The temperature and time delay prior to removal of excess prepolymer in the capillary is an important parameter, since this affects the viscosity of the prepolymer. The influence of the temperature was studied in the range from 25 °C (time needed to complete the polymer curing is ca. 24 h) up to 65 °C (time needed to complete the polymer curing is ca. 4 h). The time delay was varied from none to 30 min. The average film thickness of the traps was determined by gravimetric analysis.

2.2. Instrumental

Evaluation of the retention performance of the different traps was carried out on a 6890GC (Agilent Technologies, USA) with a split/splitless injector (100 °C) and a flame ionization detector. The trap was connected to the injector and detector via zero dead volume connectors in each end (ZRU1.5, Vici, Switzerland) followed by a short piece of deactivated fused silica tubing (ca. 20 cm × 320 μm i.d., Agilent Technologies). The GC oven temperature was kept at 27 °C. Nitrogen was used as carrier gas. Elution analysis was performed by injecting 20 μl hexane headspace using an autoinjector (G1513A, Agilent Technologies) and a gas tight syringe (50 μl, Agilent Technologies). Statistical moments

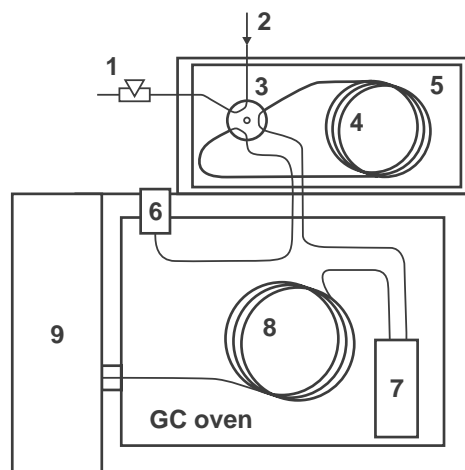


Fig. 3. A schematic of the set-up used to desorb the ITFT. The desorption mode is shown. 1 = Needle valve; 2 = auxiliary flow; 3 = six-port valve; 4 = ITFT; 5 = oven; 6 = split injector of the GC; 7 = Dewar cup for liquid nitrogen cryofocusing; 8 = separation column; 9 = mass detector.

of the peaks were calculated using Chemstation software (Agilent Technologies).

For practical application tests of the ITFTs, a gas chromatograph (6890GC, Agilent Technologies) equipped with a split/splitless injector and a quadrupole mass spectrometer (5973MSD, Agilent Technologies) was employed. The trap was placed in a small oven (simply heated with hot air from a heat-gun and temperature controlled by a Pt-100 sensor) together with an air-actuated six-port valve (A4C6WT, Vici), which was used to switch the trap in line with the separation column. A Dewar cup with liquid nitrogen was utilized to focus the desorbed analytes on the separation column. The set-up is schematically depicted in Fig. 3. The auxiliary flow (2 ml/min of helium) was used to purge the trap in the sampling flow direction for 1 min before each thermal desorption. This procedure was adapted to remove possible residual water and carbon dioxide. Desorption was performed at 100 °C for 10 min in the reversed flow direction with respect to sampling. Before use, the traps were conditioned at 170 °C under a nitrogen flow of 50 ml/min for 4 h. The chromatographic conditions were: column, HP624 (30 m × 0.32 mm i.d., film thickness 1.8 μm, Agilent Technologies); carrier gas, helium at a constant flow rate of 2.0 ml/min; oven temperature, 30 °C for 5 min and then 5 °C/min to 200 °C and kept at this temperature for 2 min. The mass detector was operated in the scan mode at 2.4 scans/s.

3. Results and discussion

3.1. Preparation of irregular thick film open tubular traps

The preparation of very thick films of stationary phase is not trivial. To apply the regular static coating method [14] would be extremely tedious, due to the very high viscosity of

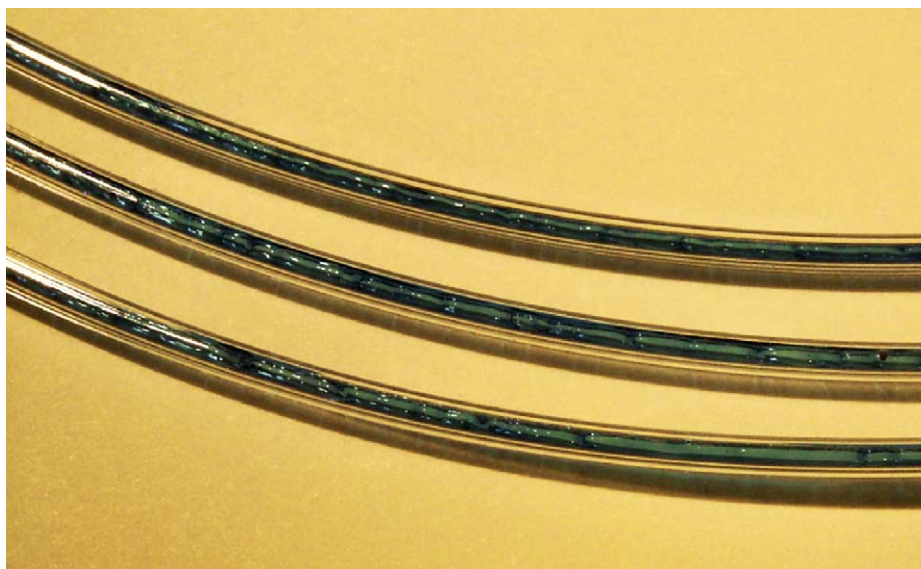


Fig. 4. Photograph of an ITFT (glass capillary). The irregular film of the stationary phase is visualized by addition of a hydrophobic blue dye to the prepolymer, prior the coating process. Trap data: 0.745 mm i.d., $\beta = 1.33$ (average film thickness 91 μm).

the coating solution. Also, the thick film has a pronounced tendency to rearrange in droplets, thereby inducing the risk of column blockage. Our earlier concept [5] of cross-linking the stationary phase immediately after formation of the thick film solves all these problems, but the technology is quite demanding. In the present method, the prepolymer is simply forced through the column by gas pressure, which leaves an irregular film of stationary phase onto the column wall. The sustained gas flow continuously disrupts droplets, thus keeping an open gas passage. An irregular film is thereby created, which is thermally immobilized in this semi-static state. Fig. 4 shows a photograph of a typical irregular thick film trap, obtained in this way.

As pointed out in Section 2, the resulting average film thickness depends on a number of variables, including the coating gas flow (pressure) as well as the viscosity of the prepolymer. The latter can be increased by a partial pre-curing, which is accomplished by raising the temperature of the coating prepolymer and/or delaying the start of the coating. The influence of the gas pressure/flow is less obvious. In certain cases, an increased pressure (gas flow) led to a decreased film thickness, but the results were not consistent. In regular dynamic coating of stationary phases, it is well known that an increased coating speed actually leads to an increased film thickness, in accordance with fundamental observations, made by Fairbrother and Stubbs [15]. In our case, the mechanisms for film formation include anomalies, related to the irregularity of the film. When the bulk volume of prepolymer has been pushed through the column, a high gas speed prevails, and numerous droplets are formed, which are continuously broken up and pushed out of the column in a wave-like way. An increased gas flow (pressure) reduces the resulting film thickness, but with high viscosity prepolymers, opposite results were observed.

In our study, we employed pressures between 20 and 200 psi, and the temperature of the prepolymer was usually not higher than 35–40 °C. This yielded an average film thickness ranging between 40 and 150 μm . Other preparation conditions can be employed to prepare traps with much thicker films. Table 1 shows some characteristics of irregular thick film traps, along with the corresponding preparation data. The table also includes data for a thick film trap with a regular, smooth coating. The film thickness of the ITFTs are average values, and were calculated by gravimetric analysis.

3.2. Performance evaluation

In order to evaluate the performance of the ITFTs, a series of elution analyses at different gas velocities with hexane as solute were carried out. The study included the three ITFTs from Table 1 as well as the OTT with the smooth, regular coating, providing a performance reference.

The peaks obtained during the tests were not fully symmetrical and to ensure an accurate peak characterization, statistical moments were therefore utilized [16]. The number of theoretical plates (N) was calculated using Eq. (1):

$$N = \frac{M_1^2}{M_2} \quad (1)$$

where M_1 is the first moment and corresponds to the elution time of the centre of gravity of the peak and M_2 the second central moment, the variance of the peak. The height equivalent to a theoretical plate ($\text{HETP} = L/N$, where L = length of trap) versus the average linear velocity was calculated for each trap and the results are shown in Fig. 5.

As can be observed, the difference in efficiency of the ITFTs compared to the regular OTT is not very large. At first sight, this may seem to be illogical, when considering

Table 1
Properties of the traps studied in detail

| | ITFT-200 ^a | ITFT-400 ^a | ITFT-345 ^b | OTT-ref ^c |
|-----------------------------|-----------------------|-----------------------|-----------------------|----------------------|
| Pre-cure temperature (°C) | 30 | 30 | 35 | – |
| Pre-cure time (min) | 20 | 10 | 10 | – |
| Coating pressure (psi) | 40 | 100 | 80 | – |
| Length (cm) | 200 | 400 | 345 | 155 |
| Internal diameter (mm) | 0.762 | 0.762 | 0.734 | 0.718 |
| Average film thickness (μm) | 84.2 | 105.5 | 114 | 91 |
| β | 1.54 | 1.1 | 0.91 | 1.26 |

^a Silcosteel capillary.

^b Glass capillary.

^c Trap with regular film prepared as described by Blomberg and Roeraade [5].

the extraordinary importance of film uniformity for obtaining GC capillary columns with a good coating efficiency (i.e. high plate numbers). However, thick film open tubular traps have an extremely large HETP (in the order of decimetres) which is totally due to the excessive resistance to mass transport in the stationary phase, and the relative influence of the coating uniformity (the added peak variance) is therefore far less.

Open tubular traps are designed for analyte enrichment, and not for molecular separation. Therefore, the relevance of their chromatographic properties is different. For direct quantitative trapping, the relation between breakthrough volume, pressure drop and sampling flow rate are issues of central importance. Essentially, the volume of the stationary phase and the geometry of the trap are the most significant parameters to optimize. The efficiency in terms of plate numbers is less important and should basically only be kept above a reasonable level. Lökvist and Jönsson [17] have compared several models describing the breakthrough curves of sampling traps with low number of plates. They

suggested the use of Eq. (2) to predict breakthrough volumes:

$$V_b = V_R \left(0.9025 + \frac{5.360}{N} + \frac{4.603}{N^2} \right)^{-1/2} \quad (2)$$

This equation is actually an applied model of the general version, where the breakthrough volume (V_b) in this applied model is assumed to include a 5% breakthrough loss of analyte; V_R is the retention volume. Using this model, the breakthrough volume will be 92% of V_R for $N = 20$ while values of $N = 10$ and 5 yield 82 and 68%, respectively. Lowering N from 20 to 5, will therefore only decrease the breakthrough volume by approximately 26%.

In order to study the loss in efficiency as a result of having irregular film coatings, linear regression analysis was applied to the HETP curves in Fig. 5. The analysis revealed that the irregular film coating resulted in an approximately 30% increase of the HETP. For a given trap length, this is equivalent to a decrease in N of roughly 23%. In the light of this discussion, it can therefore be expected that the influence of this moderate reduction in efficiency on the breakthrough volume will be rather insignificant.

In order to verify this assumption, the breakthrough characteristics of the traps were compared, where Eq. (2) was

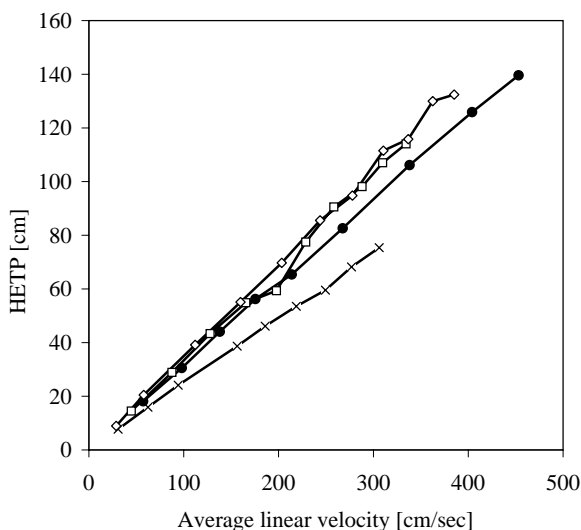


Fig. 5. HETP curves for the selected traps. (x) Reference trap with smooth film coating; (●) ITFT-200 trap; (◇) ITFT-345 trap; (□) ITFT-400 trap. See Table 1 for corresponding data.

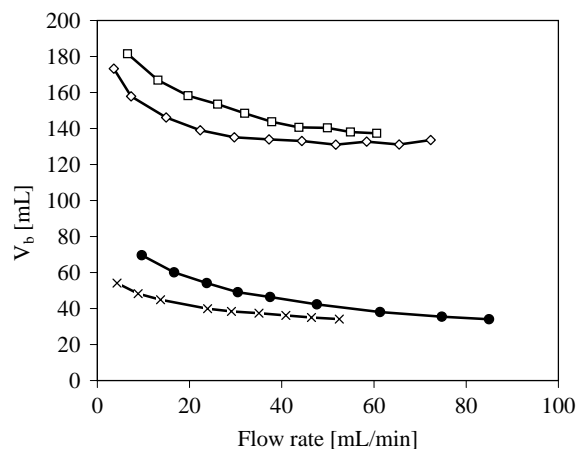


Fig. 6. Breakthrough volumes vs. flow rate for the selected traps. (x) Reference trap with smooth film coating; (●) ITFT-200 trap; (◇) ITFT-345 trap; (□) ITFT-400 trap. See Table 1 for corresponding data.

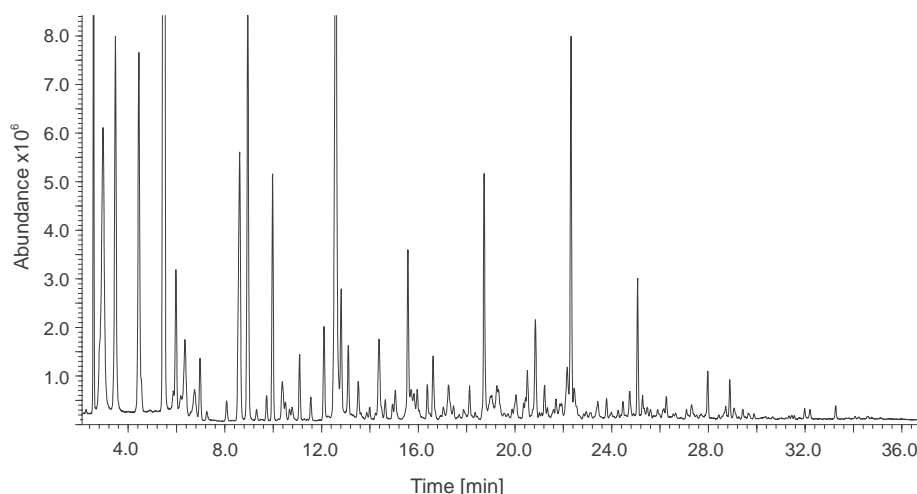


Fig. 7. Chromatogram of headspace (50 ml) from brewed coffee, trapped on the ITFT-200 (for data see Table 1). The sample was collected at room temperature at 5 ml/min. For further experimental conditions, see text.

utilized together with the elution analysis data (values of V_R and N for hexane). The results are displayed in Fig. 6. This revealed that the OTT, in spite of its smooth film coating, has the smallest breakthrough volume, which is due to the fact that this trap contains the least amount of stationary phase (292 mg). The 200 cm long ITFT is coated with 376 mg of PDMS and has a slightly higher breakthrough volume. With the longer traps, a quantitative enrichment of traces of hexane can be performed within a few minutes from a gaseous sample of more than 130 ml. When analysing environmental air (containing water), this is not feasible with conventional headspace technology and cryofocusing.

An interesting observation is that the breakthrough volume does not decrease to any major extent when the flow rate is significantly increased. Thus, fast sampling procedures can be implemented and performance is hardly sacrificed. The only issue of concern is the increase in pressure drop, which must be <1 bar if the sample is pulled through the trap by suction. We found that the difference in pressure drop characteristics between the ITFT and the smooth film OTT were insignificant.

In principle, any cross-linkable polymer can be utilized for preparing ITFTs, but good diffusive properties of the polymer are important. In this respect, PDMS is a very favourable choice. More polar polymers would provide a better retention of polar solutes, which is quite poor in the case of PDMS. However, polar stationary phases also have more affinity for water, which leads to complications in both the trapping and the subsequent analysis step. In a forthcoming paper, we will describe a way to deal with this problem.

To test the practical performance of the ITFTs, volatiles from a 50 ml headspace of brewed coffee (room temperature) were trapped and analyzed. Under these conditions, a quantitative determination of hexane and any other components with the same or larger partition coefficients is obtained. The results are shown in Fig. 7. This headspace sample is saturated with water vapour, but the ITFT concentrate

could be cryofocused on the separation column without any complications. It should be mentioned that thermal desorption of the ITFTs can also easily be performed by passing a direct current through the steel mantle of the traps, which further simplifies the overall set-up.

4. Conclusions

A method for preparation of thick film traps with an irregular coating of stationary phase is described. The procedure is very simple and rapid, and allows any average laboratory to produce large numbers of cheap open tubular sorption traps. The characteristics of the traps are low pressure drop, while the performance in terms of efficiency is only ca. 30% lower than conventional traps with smooth, thick films. In terms of breakthrough volume, the difference in performance is marginal.

Acknowledgements

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References

- [1] N.H. Snow, G.C. Slack, Trends Anal. Chem. 21 (2002) 608.
- [2] C. Arthur, J. Pawliszyn, Anal. Chem. 62 (1990) 2145.
- [3] E. Baltussen, P. Sandra, F. David, C.A. Cramers, J. Microcol. Sep. 11 (1999) 737.
- [4] E. Baltussen, H.-G. Janssen, P. Sandra, C.A. Cramers, J. High Resolut. Chromatogr. 20 (1997) 385.
- [5] S. Blomberg, J. Roeraade, J. High Resolut. Chromatogr. Chromatogr. Commun. 11 (1988) 457.
- [6] S. Blomberg, J. Roeraade, J. High Resolut. Chromatogr. 12 (1989) 138.

- [7] B.V. Burger, A.E. Nell, W.G.B. Petersen, J. High Resolut. Chromatogr. 14 (1991) 718.
- [8] C. Bicchi, A. D'Amato, F. David, P. Sandra, J. High Resolut. Chromatogr. 12 (1989) 316.
- [9] B.V. Burger, M.E. Le Roux, Z.M. Munro, M.E. Wilken, J. Chromatogr. 552 (1991) 137.
- [10] B.V. Burger, Z. Munro, J. Chromatogr. 370 (1986) 449.
- [11] S. Blomberg, J. Roeraade, J. Chromatogr. 394 (1987) 443.
- [12] B.V. Burger, M. Le Roux, W.J.G. Burger, J. High Resolut. Chromatogr. 13 (1990) 777.
- [13] E.K. Ortner, E.R. Rohwer, J. High Resolut. Chromatogr. 19 (1996) 339.
- [14] J. Bouche, M. Verzele, J. Gas Chromatogr. 6 (1968) 501.
- [15] F. Fairbrother, A.E. Stubbs, J. Chem. Soc. (1935) 527.
- [16] J.P. Foley, J.G. Dorsey, Anal. Chem. 55 (1983) 730.
- [17] P. Lövkvist, J.Å. Jönsson, Anal. Chem. 59 (1987) 818.