Solvent-enhanced headspace sorptive extraction in the analysis of the volatile fraction of matrices of vegetable origin

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Abstract

The solvent-enhanced headspace sorptive extraction (SE-HSSE) technique aims to modify PDMS polarity using a solvent to increase its concentration capability. In SE-HSSE, a PDMS tubing closed at both ends by small glass stoppers and filled with an organic solvent is suspended in the sample headspace for a fixed time. After sampling, the sampled analytes are recovered from the PDMS tubing by thermal desorption and on-line transferred to a GC-FID or GC-MS system for analysis. Cyclohexane, iso-octane, ethyl acetate, acetone, acetonitrile and methanol were tested as PDMS modifiers to sample the volatile fractions of sage (*Salvia lavandulifolia* Vahl.), thyme (*Thymus vulgaris* L.) and roasted coffee. Ethyl acetate was found to be the most effective PDMS modifier for all matrices investigated; although to a lesser extent, cyclohexane also increased component recoveries with sage and thyme. Acetone, acetonitrile and methanol did not increase PDMS recovery while isooctane was excluded because of its interaction with the polymer. The results show that solvent-modified PDMS extends the range of sampled headspace components with different polarities, increases the recovery of many of them, improves sensitivity in trace analysis, speeds-up recovery and gives a repeatability comparable to that of unmodified PDMS.

Keywords: Headspace sampling, Solvent enhanced HeadspaceSorptive Extraction (SE-HSSE); PDMS tubing, solvent-modified-PDMS polarity, GC-MS, vegetable matrices

1. Introduction

High concentration capacity headspace (HCC-HS) techniques are sampling approaches in which the analytes in the vapour phase are concentrated into a sorbent, an adsorbent or a solvent. The best known HCC-HS technique is solid phase microextraction (SPME),

which was introduced by Arthur and Pawliszyn in 1990 for liquid sampling [1] and extended to HS sampling by Zhang and Pawliszyn in 1993 [2]. Since then, several new techniques have been introduced, with the aim of improving the performance achievable by SPME and extending the fields of application; they were recently discussed critically in a review on headspace sampling by Bicchi et al. [3]. Stir bar sorptive extraction (SBSE) [4] and headspace sorptive extraction (HSSE) [5,6] are fully-sorption-based sample preparation techniques that have been successfully applied to recover target analytes from complex matrices in both liquid and vapour phase [7-9]. Stir bars (also known as "Twisters®") consist on a very thick PDMS film coated on a glass-coated magnetic stir bar, where the analytes are recovered from both a liquid or vapour phase. One of the main drawbacks of sorptive techniques is that they are almost exclusively based on the use of polydimethylsiloxane (PDMS) as extracting polymer, thus making difficult to recover polar and/or highly volatile analytes from complex matrices, and/or sometimes discriminating among/against them. The most effective solution for medium-to-highly polar compounds would be to find a polar polymer to coat twisters with the same sorptive properties as PDMS, but at the same time with a better affinity for low $K_{O/W}$ (octanol/water partition coefficient) compounds (i.e. log $K_{O/W}$ <2.0). In analogy to SPME, polyacrylate has been tested as sorptive material for twisters, but was abandoned because of its low reproducibility and high bleeding rate. Several other attempts have been made to find new coating materials for twisters [7] but, at present, a polar polymer with performance comparable to that of PDMS for apolar or moderately polar compounds has yet to be found. Two approaches are to date available in this respect: 1) extending the polarity of PDMS devices and, as a consequence, their sorptive properties [7] and 2) modifying the polarity of target analytes through suitable derivatisation processes to make them more compatible with PDMS. This latter topic is outside the scope of this

article: a short and non-exhaustive survey concerning it as applied to SBSE is reported in reference [7].

One of the approaches proposed to modify twister sorptive properties is to combine PDMS with one or more other sampling materials accumulating analytes in different modes (e.g. adsorption), introduced by Bicchi et al. in 2005 and successfully used for sampling target components in several matrices in liquid and vapour phases [10]. The resulting dual-phase twisters (DP-Twisters) consist of a short PDMS tube (1-2 cm long) the ends of which are closed with two magnetic stoppers, thus creating an inner cavity that can be packed with different sorts of adsorbents. The concentration capability of DP-twisters for each analyte is therefore the result of the analyte's sorption onto PDMS from liquid or vapour phase, followed by its diffusion through the PDMS layer and adsorption (or sorption) onto the inner phase. Several different PDMS and inner-phase materials have been investigated and applied to both standard mixtures and real-world samples. The most effective adsorbents were found to be Carbopack B, Tenax GC, a bisphenol-PDMS copolymer and Carbopack coated with 5% of Carbowax [11].

PDMS concentration capability can also be improved with the help of a solvent. With this approach, analytes are concentrated into an organic solvent stored inside a short piece of PDMS tubing sealed at one end and suspended in the aqueous sample so that they can diffuse through the PDMS, which acts as a selective non-porous membrane, and concentrates them into the inner solvent by sorptive extraction. Lehotay et al. [12-14] introduced Solvent in Silicone Tube Extraction (SiSTEx) as an approach to be combined with the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method to reduce the detection limit of 26 pesticides analysed at the ppb level, using acetonitrile as inner solvent in PDMS tubing, in combination with GC-MS. Sandra et al. [15-17] introduced Silicon Membrane Sorptive Extraction (SMSE), and used ethyl acetate as

solvent to concentrate and then quantify atrazine and its three metabolites in water samples in the 1-10 ppt range by GC-SIM-MS and LC-MS. Van Hoeck also investigated the influence of ethyl acetate as inner PDMS solvent on recovery of EDCs (endocrine disrupters) and pharmaceuticals of different polarity ($K_{o/w}$ between 0 and 4) from a salted-out standard solution at the ppt level and found that SMSE was more effective than SBSE only for very polar compounds ($K_{o/w} < 2$) [18]. Hauser et al. [19,20] and Schellin et al. [21-23] applied the same approach (Membrane Assisted Solvent Extraction - MASE) in a fully-automatic analysis system using a tubing of dense polypropylene as "sorptive" membrane medium, filled with 500 - 800 µL of hexane or cyclohexane as acceptor solvent, and triazines, 2,4-dichloroanilines, α-HCH and phenanthrene as model compounds; the resulting solution was then on-line analysed by large-volume-injection GC-MS [19]. They also applied this technique to determine polychlorinated biphenyls [20], organophosphorus pesticides as such [21] or together with triazines and organochlorine compounds [22] in several real-world water samples and other matrices. Isolation of the sample solution from an immiscible extraction solvent and, as a consequence, from the extracted analytes can also be achieved by microporous membrane-liquid-liquid extraction (MMLLE). This approach was first adopted to increase the sensitivity of liquid-phase microextraction (LPME) [24,25] and to stabilize the solvent drop using a microporous polypropylene hollow fibre assembled on a cone tip microsyringe open at the bottom and impregnated with an organic hydrophobic solvent as an interface between analyte acceptor (organic solvent) and donor phases (water sample) [26-28]. LPME, and in particular its automation and optimization in combination with gas chromatography, was recently reviewed by Ouyang et al [29].

Solvents can also be associated to PDMS to increase the effectiveness of HS sampling. In this case, the inner solvent is not used as an acceptor of the analytes recovered from the

vapour phase through the PDMS membrane, but acts as a modifier of the polarity of the PDMS through which it diffuses, extending the range of the analyte polarities that can be sampled with high recovery. The sampled analytes are therefore accumulated in the PDMS, and then recovered by thermal desorption and on-line analyzed by GC or GC-MS. This article reports the results of a study aiming to apply sorptive extraction with solvent modified PDMS to HS sampling (Solvent enhanced-Headspace sorptive extraction SE-HSSE) and to evaluate the effectiveness of PDMS modified with different solvents to sample the volatile fraction of a group of matrices of vegetable origin (sage, *Salvia lavandulifolia* Vahl., and thyme, *Thymus vulgaris* L.) and roasted coffee. Six solvents were tested as modifiers of PDMS polarity i.e. cyclohexane, iso-octane, ethyl acetate, acetone, acetonitrile and methanol, and the effect of the parameters influencing sampling effectiveness was investigated.

2. Experimental

2.1 Materials and Reagents

Homogeneous samples of dried sage leaves (*Salvia lavandulifolia* Vahl.) and dried thyme leaves (*Thymus vulgaris* L.) were from the University of Turin Botanical Gardens. Ground coffee samples were 100% Arabica originating from Costarica. Solvents (ethyl acetate, iso-octane, acetone, methanol, acetonitrile, cyclohexane) were all pesticide-grade from Riedel-de Haen (Seelze Germany). PDMS tubing (4 cm long, 1.5 mm i.d., and 0.5 mm thick) were purchased from Gerstel (Mülheim a/d Ruhr, Germany).

2.2 Evaluation of PDMS-solvent impregnation

Eight PDMS tubings of the same dimension and weight, originating a total inner volume of about 150 µL, were loaded respectively with 120 µL of ethyl acetate, acetone,

acetonitrile and methanol, and 20 and 120 µL of cyclohexane and isooctane; the PDMS tubings were sealed at both ends with glass beads, and stored in 20 mL HS vials at 50°C for different times (0, 5, 10, 15, 20, 25, 30, and 35 min). With methanol and acetonitrile, the tests were limited to three times (0, 20 and 40 minutes). At the time scheduled, the residual volume of solvent inside the PDMS tubing was recovered and measured with a microsyringe, each tubing was then quickly transferred to a new and exactly weighed vial, which was immediately sealed and then weighed on the analytical balance. An empty PDMS tubing of the same dimension was also weighed and taken as reference. Each experiment was repeated three times.

2.3 SE-HSSE sampling

Portions of PDMS tubing closed at both ends with small glass beads were filled with the organic solvents under investigation. The solvent-impregnated PDMS tubing was suspended using either harmonic stainless steel wire or a Gerstel special insert (Gerstel Part N° 012492-000-00) in the sample headspace for a fixed time. Figure 1 reports a diagram of the PDMS tubing and HS-sampling system. After sampling, the PDMS tubing was thermally desorbed via a TDS or TDU system (Gerstel) and the fraction recovered introduced on-line into a GC-FID or GC-MS system for analysis. The residual volumes of solvent in the PDMS tubing were analyzed by GC-MS.

Sample amount: 20 mg for sage, 10 mg for thyme, 50 mg for coffee. Vial volume: 20 mL. Sampling temperature: 50°C. Sampling time: 20 min. Solvent volume: cyclohexane: 20 µL; ethyl acetate, acetone, acetonitrile, methanol: 120 µL.

All analyses were run in triplicate. Empty PDMS tubings of the same dimensions and submitted to the same sampling conditions with the same matrices were used as references to evaluate the performance of the solvent-modified PDMS device.

2.4 Repeatability

Repeatability was evaluated on five analyses for each matrix investigated carried out under the same conditions as reported above.

2.5 SE-HSSE-thermal desorption–GC and GC-MS analysis

GC-FID unit: Agilent 5890 series II (Agilent, Little Falls, DE, USA) equipped with a TDS system (Gerstel, Mülheim a/d Ruhr, Germany).

GC-MS unit: Agilent 6890 GC- 5973 MS system (Agilent, Little Falls, DE, USA) equipped with a MPS2 autosampler and a TDU system (Gerstel, Mülheim a/d Ruhr, Germany).

Column: FSOT OV-1 (Mega, Legnano (Milan), Italy) df 0.25 µm, i.d. 0.25 mm, l 25 m for sage and thyme and MEGAWAX (Mega) df 0.25 µm, i.d. 0.25 mm, l 25 m for coffee.

Analysis conditions

TDS/TDU conditions: desorption: from 40°C to 250°C (5 min) at 60°C/min; flow mode: splitless; transfer line: 250°C. *Injection system:* Gerstel CIS-4 PTV injector, cryogenic fluid: CO_2; split mode, split ratio 1:10, injection temperature: from –50°C to 280°C (5 min) at 600°C/min; *Oven:* temperature programme: sage and thyme: from 50°C (1 min) to 180°C at 3°C/min then to 270°C (5 min) at 20°C/min; coffee: from 20°C (2 min) to 40°C at 5°C/min, to 180°C at 3°C/min then to 220°C (5 min) at 5°C/min. *Carrier gas*: helium; flow-rate: 1.0 mL/min in constant flow mode.

MS conditions: MS was in EI mode at 70 eV. Ion source temperature: 250°C. The HS components were identified by comparison of their mass spectra with those of authentic samples or with data from Nist05 and Adams mass spectral databases [30,31].

2.6 Inner solvent GC-MS analysis

The inner solvent recovered after SE-HSSE sampling was analyzed under the same conditions reported for PDMS tubing, except that it was injected by conventional split splitless injector. Injection conditions: mode: split, split ratio: 1:10; temperature: 250°C; volume: 1 µL.

3. Results and Discussions

This study aimed to evaluate how a solvent inside PDMS tubing can influence its recovery capability when used to sample the headspace of the volatile fraction of matrices of vegetable origin. Two main topics were investigated: a) the influence of the nature of the modifying solvent on PDMS impregnation and recovery, and b) the application of solvent-modified PDMS to headspace sampling and the influence on its composition.

In vapour phase solvent-modified PDMS sorptive extraction sampling (SE-HSSE), the inner solvent acts as modifier of the polarity of the PDMS tubing from which the analytes are recovered, unlike in liquid-phase SMSE (LP-SMSE), where the inner solvent accumulates the analytes that have diffused through the PDMS, which operates as a selective membrane. In SE-HSSE, the analytes have therefore to be recovered from the PDMS tubing by thermodesorption before on-line analysis by GC-MS, while in LP-SMSE, the inner solvent is on-line or off-line injected into the GC-MS system.

3.1. PDMS solvent-impregnation and nature of the solvent

In SE-HSSE, the inner solvents diffuse through the PDMS, impregnate it to saturation, and evaporate into the headspace, the entity of the whole process obviously depending on the nature of the solvent. A series of experiments was therefore carried out to determine the approximate amount (volume) of solvent impregnating PDMS over time, and its

residual volume in the tubing. The following solvents were tested: cyclohexane, iso-octane, ethyl acetate, acetone, acetonitrile and methanol. Isooctane produced severe PDMS swallowing with all tested volumes (20-120 µL), making its use for HS-sampling impossible. It was therefore eliminated immediately from the solvents investigated.

The experiments (paragraph 2.2) with cyclohexane, ethyl acetate and acetone were run for eight different times (0, 5, 10, 15, 20, 25, 30, and 35 min) while those with methanol and acetonitrile were limited to three times (0, 20 and 40 min), because preliminary experiments showed that their inner volume inside the tubing was almost constant at all times considered. The volume of solvent impregnating the PDMS was calculated from the following expression:

$$V_{SolvPDMS} = (W_{PDMS+Solv} - W_{PDMS})/d$$

where $V_{SolvPDMS}$ is the volume of solvent impregnating PDMS, $W_{PDMS+Solv}$ is the weight of the PDMS emptied of the residual solvent, W_{PDMS} is the weight of the untreated PDMS tubing and d the density of the investigated solvent.

Figure 2 reports the variations over time both of the volume of each solvent impregnating PDMS tubing and of the residual volume inside the tubing. Under the same conditions and sampling time, the tested solvents behaved differently depending on their volatility and affinity to PDMS: i) cyclohexane (120 µL) totally diffused through the PDMS in about five minutes and impregnated it with about 90 µL. Cyclohexane likewise produced considerable swallowing of the polymer, less evident than that of isooctane, but nevertheless sufficient to make this volume unusable for HS-sampling. Moreover, at the sampling temperature (50°C), with 120 µL, the solvent evaporated into the headspace, condensed on the vial glass walls, and impregnated or "wetted" the solid matrix, thus

interfering with the headspace composition. In view of its use for HS-sampling, the amount of cyclohexane was therefore drastically reduced from 120 to 20 μL; ii) ethyl acetate (120 μL) also impregnated PDMS in a high amount (about 75 μL) but the liquid phase persisted for longer in the tubing (about 20 minutes), iii) acetone (120 μL) impregnated PDMS in lower amounts (about 10 μL), its volume inside the tubing decreasing slowly for 20 minutes, remaining constant thereafter (about 25 μL), and iv) acetonitrile and methanol persisted inside the PDMS tubing throughout the sampling time in high volumes (about 90 and 85 μL, respectively), and only small volumes impregnated the PDMS (4 and 5 μL, respectively).

Under these conditions, the performance of the investigated PDMS tubings was highly repeatable for several consecutive samplings (at least 50) without alteration of its recovery capability.

Although approximate, these results indicatively show that a) different volumes of each solvent impregnate PDMS to different extents depending on their nature, b) the volume of solvent impregnating PDMS achieves equilibrium within a few minutes, c) after equilibration, the volume of solvent in the PDMS remains fairly constant throughout the sampling time, meaning that its contribution to PDMS polarity (and as a consequence to its concentration capability) is constant, and d) the missing solvent is mostly vaporized from PDMS to the headspace.

3.2 SE-HSSE sampling

The SE-HSSE performance was evaluated by determining the influence of each solvent on the PDMS recovery of a set of selected markers with different chemical structures characteristic of three matrices: sage (*Salvia lavandulifolia* Vahl.), thyme (*Thymus vulgaris* L.) and coffee (*Coffea arabica* L). Each matrix was submitted to SE-HSSE

sampling for 20 min at 50°C with PDMS tubings modified with each of the solvents investigated.

The effect of the solvent on the SE-HSSE sampling capability was determined through its contribution to analyte recovery ("solvent contribution"), expressed as ΔRA%, i.e. the percentage variation in the abundance of a given component (i) obtained with the solvent-modified PDMS tubing calculated *vs.* an empty PDMS tubing, with the following equation (2):

$$\Delta RA\% = [(A_{i(PDMS+solvent)} - A_{i(emp)})/A_{i(emp)}] \times 100 \quad (2)$$

where $A_{i(PDMS+solvent)}$ is its peak area obtained with a solvent-modified-PDMS tubing and $A_{i(emp)}$ that with the corresponding empty PDMS tubing.

Table 1 reports the average ΔRA% calculated on three repetitions for the markers of thyme, sage and coffee after sampling with PDMS tubing modified with each of the solvents investigated.

Figure 3 reports the SE-HSSE-GC-MS profiles of the headspace of a dried sage leaves sample obtained with an empty and a cyclohexane-modified PDMS tubings.

Figure 4 reports the SE-HSSE-GC-MS profiles of the headspace of a roasted Arabica coffee sample obtained with empty and with ethyl acetate-modified PDMS tubings. These experiments showed that ethyl acetate and cyclohexane were very effective PDMS modifiers for the HS sampling of sage and thyme, compared to PDMS as such (Table 1, Figure 3), while the other solvents did not improve analyte recovery. On the other hand, with coffee a marked increase in recovery was only obtained with ethyl acetate, probably due to its closer affinity to the polarity of coffee HS components (Figure 4). The high ΔRA% of acetic acid is not significantly influenced by the amount from ethyl acetate

hydrolysis, as it is evident from sage and blank chromatograms where it is present as a trace.

Acetone, methanol and acetonitrile did not make significant contribution to analyte recovery with any of the matrices, partly because very low volumes of solvent impregnated the PDMS. The residues of acetone, acetonitrile and methanol recovered from the PDMS tubing after sampling were also analyzed by GC-MS to check whether PDMS may act as a selective membrane also in vapour phase sampling, but no components characterizing the headspace of the matrices under study were found in detectable amounts in any of the solvents in question. These results show that i) the solvents positively acting on PDMS concentration capability are those more compatible with PDMS, i.e. those effectively impregnating it (ethyl acetate and cyclohexane); ii) those solvents increasing the polarity of PDMS contribute more effectively to the recovery of the more polar compounds, and that iii) in SE-HSSE, analytes are accumulated in the PDMS, unlike what occurs in SMSE. On the contrary, the permeability of PDMS to the solvent (and as a consequence the modification of PDMS by the solvent) must be low for PDMS to act as a membrane, to enable analyte accumulation in the inner solvent (i.e. acetonitrile, methanol).

3.2.1. Solvent-modified PDMS vs. recovery over time and inner solvent volume

The influence of sampling time on solvent-modified PDMS tubing was also studied with the most effective modifier(s) for each sample, i.e. cyclohexane and ethyl acetate for sage and thyme; and ethyl acetate for coffee. The variation over time (1, 5, 10, 20 and 40 minutes) of solvent contribution (ΔRA%) to recovery vs. an empty PDMS tubing was determined. Figure 5 shows how the extraction time influences the HS recovery of markers with different structure, polarity and volatility from the matrices investigated

with the solvent-modified PDMS tubings: in particular 1,8-cineole and camphor from sage and thymol and p-cymene from thyme, with cyclohexane- and ethyl acetate-PDMS, and pyridine and acetic acid from coffee, with ethyl acetate-PDMS. With sage, ethyl acetate was the most effective solvent for both markers, producing the greatest increase of relative abundance *vs.* an empty PDMS tubing after five minutes for 1,8-cineole, and after ten minutes for camphor. With cyclohexane, both compounds achieved their maximum increase in five minutes. With thyme, ethyl acetate is again the most effective modifier, but the effect was less than with sage, and the trend of increase in recovery of p-cymene and thymol with both solvents was almost constant over all sampling times. With coffee, again the greatest increase in recovery of acetic acid and pyridine was obtained within the first five minutes. These results show that the modifying solvent also influences the speed of analyte recovery.

The influence of the initial volume of solvent on SE-HSSE recovery was also evaluated, by sampling sage headspace with PDMS tubing to which 20, 60 or 120 µL of ethyl acetate had been added. Ethyl acetate was investigated since the above results showed that it is not only effective but also enables the use of different impregnating volumes. The amounts of ethyl acetate impregnating PDMS, calculated as reported in section 3.1, were respectively 7 µL with 20 µL, 26 µL with 60 µL and about 75 µL with 120 µL. The results reported in table 2 show that the volume of solvent impregnating PDMS affects recoveries markedly, in particular with the most volatile components, and this further demonstrates that the solvent greatly affects the PDMS concentration capability.

3.2.2 Repeatability

The repeatability of solvent-modified PDMS tubings was evaluated across five replicates for each matrix investigated. Table 1 reports repeatability and the relative standard deviations (RSD%) of the markers of the volatile fraction of thyme and sage, using ethyl

acetate and cyclohexane and coffee with ethyl acetate as PDMS modifiers. The repeatability obtained with an empty PDMS tubing of the same dimensions and weight is included as a reference. The technique showed good repeatability with all solvents, RSD% never exceeding 14 % with either ethyl acetate (13.7% carvacrol in sage, 13.5% thymol in thyme, and 13.7% pyridine in coffee) or cyclohexane (12.3% 1,8-cineole in sage and 13.7% borneol in thyme).

3.3. Concluding remarks

Solvent-modified PDMS sorptive extraction (SE-HSSE) was here applied to headspace sampling of a group of matrices of vegetable origin (sage, thyme and coffee), showing that PDMS concentration capability can successfully be improved through modifying its polarity by means of a solvent. Among the six solvents investigated (i.e. cyclohexane, iso-octane, ethyl acetate, acetone, acetonitrile and methanol) ethyl acetate was found to be the most effective PDMS modifier for all matrices; although to a lesser extent, cyclohexane also increased component recoveries with sage and thyme. The results of the experiments on PDMS impregnation and recovery (section 3.2 and 3.3) appear to indicate that cyclohexane mainly influences polymer reticulation (or the physical structure of the polymer) while ethyl acetate effectively acts on its polarity. These results also show that PDMS concentration capability can successfully be modified only by those solvents effectively impregnating it (ethyl acetate and cyclohexane).

This simple and effective approach to modifying PDMS polarity provides the following advantages: a) the range of sampled headspace components with different polarities is extended, b) recovery of many of them is increased *versus* that obtained by conventional PDMS tubing, c) sensitivity for trace analysis is improved, d) recovery is speeded up,

with repeatability comparable to that of unmodified PDMS. Further studies are under way to evaluate the effectiveness of SE-HSSE for trace quantitation.

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Captions to figures

Figure 1 - Diagram of SE-HSSE sampling and of the PDMS tubing.

Figure 2 - Variations of i) volume of each investigated solvent impregnating PDMS tubing over time (2a, 2c, 2e) and ii) residual solvent volume inside the tubing (2b, 2d, 2f). 2a, 2b cyclohexane (20µL); 2c, 2d ethyl acetate and acetone (120 µL); 2e, 2f acetonitrile and methanol (120 µL).

Figure 3 - SE-HSSE-GC-MS profiles of the headspace of a dried sage leaves sample obtained with empty and cyclohexane-modified PDMS tubing (for analysis conditions see text). Peak identification: (1) 1,8-Cineole; (2) Camphor; (3) Borneol; (4) Terpinen-4-ol; (5) α-Terpineol; (6) Bornyl acetate; (7) Thymol; (8) Carvacrol; (9) α-Cubebene; (10) β-Caryophyllene; (11) α-Humulene.

Figure 4 - SE-HSSE-GC-MS profiles of the headspace of a roasted Arabica coffee sample obtained with empty and ethyl acetate-modified PDMS tubing (for analysis conditions see text). Peak identification: (1) Pyridine; (2) Pyrazine, 2-Methyl; (3) Pyrazine, 2,5-Dimethyl; (4) Pyrazine, 2,6-Dimethyl; (5) Pyrazine, 2-Ethyl-5-Methyl; (6) Acetic Acid; (7) Furfural; (8) Furfuryl acetate; (9) Furfuryl alcohol; (10) Pyrazine, 2-Acethyl-3-Methyl; (11) Phenol, 2-Methoxy; (12) Phenol, 4-Ethyl-2-Methoxy; (13) Phenol, 2-Methoxy-4-Vinyl.

Figure 5 - Influence (ΔRA% solvent-modified-PDMS/empty-PDMS tubings) of extraction time on HS recovery of 1,8-cineole and camphor from sage, and of thymol and

p-cymene from thyme, with PDMS tubings modified with cyclohexane and ethyl acetate (5a and 5b) and of pyridine and acetic acid from coffee with ethyl acetate (5c).

Table 1 Average ΔRA% and repeatability (RSD%) compared to an empty PDMS tubing (Emp.) for the markers of thyme, sage and coffee after sampling with PDMS modified with ethylacetate (EtAc) and cyclohexane (CyHex).

Sage						***Thyme***						***Coffee***			
	ΔRA%		***Repeatabilty RSD%***				***ΔRA%***		***Repeatabilty RSD%***				***ΔRA%***	***Repeatabilty RSD%***	
Compound	EtAc	CyHex	Emp.	EtAc	CyHex	Compound	EtAc	CyHex	Emp.	EtAc	CyHex	Compound	EtAc	emp	EtAc
1,8-cineole	**4236**	**613**	3,0	11,1	12,3	*p*-cymene	**200**	**44**	0,2	6,7	5,7	pyridine	**1262**	5,6	13,7
camphor	**1183**	**135**	4,5	12,4	6,3	1,8-cineole	**291**	**64**	1,4	13,3	8,6	pyrazine, 2-Methyl	**539**	1,2	10,0
borneol	**302**	**75**	5,2	7,5	6,9	limonene	**551**	14	8,1	9,2	9,1	pyrazine, 2,5-diMethyl	**401**	7,7	4,6
terpinen-4-ol	**48**	**59**	5,0	5,5	9,1	γ-terpinene	**143**	**119**	0,9	7,3	6,5	pyrazine, 2,6- diMethyl	**734**	4,7	3,9
α-terpineol	**109**	**35**	6,7	11,3	9,9	*t*-sabinene hydrate	**126**	**33**	6,4	11,6	7,0	pyrazine, 2-Ethyl-5-Methyl	**167**	4,1	4,7
bornyl acetate	**287**	**81**	12,5	9,2	5,8	α-terpinolene	**540**	-2	2,7	7,6	7,9	acetic acid	**1326**	1,1	11,9
thymol	**95**	**44**	5,7	n.d.	11,6	linalool	**64**	**41**	6,0	8,9	7,7	furfural	**803**	4,6	3,5
carvacrol	-30	4	5,6	13,7	12,1	menthone	**61**	-6	1,2	12,1	5,9	furfuryl acetate	**752**	9,6	4,2
α-cubebene	4	**77**	1,5	12,5	7,1	borneol	**160**	9	10,5	8,6	13,7	furfuryl alcohol	**838**	5,5	3,9
β-caryophyllene	**95**	**87**	10,0	12,9	8,3	thymol	-2	7	8,3	13,5	8,7	pyrazine, 2-Acetyl-3-Methyl	**125**	7,9	5,4
α-humulene	**56**	**50**	7,3	8,5	10,7	β-caryophyllene	2	**20**	4,6	12,8	6,7	phenol, 2-OMethyl	-14	11,9	9,2
												phenol, 4-Ethyl,2-OMethyl	-85	1,0	5,1
												phenol, 2-OMethyl-4-vinyl	**78**	2,2	10,7

Table 2 Influence of volume of solvent impregnating PDMS on recoveries of sage markers

	ΔRA%		
	EtAc 20μL	*EtAc 60μL*	*EtAc 120μL*
1,8-cineole	**1424**	**1708**	**4236**
camphor	**198**	**277**	**1183**
borneol	**32**	**74**	**302**
terpinen-4-ol	**17**	**54**	**48**
α-terpineol	**5**	**45**	**109**
bornyl acetate	**31**	**78**	**287**
thymol	**12**	**-14**	**95**
carvacrol	**-22**	**-10**	**-30**
α-cubebene	**14**	**8**	**4**
β-caryophyllene	**77**	**83**	**95**
α-humulene	**37**	**45**	**56**

Figure 1

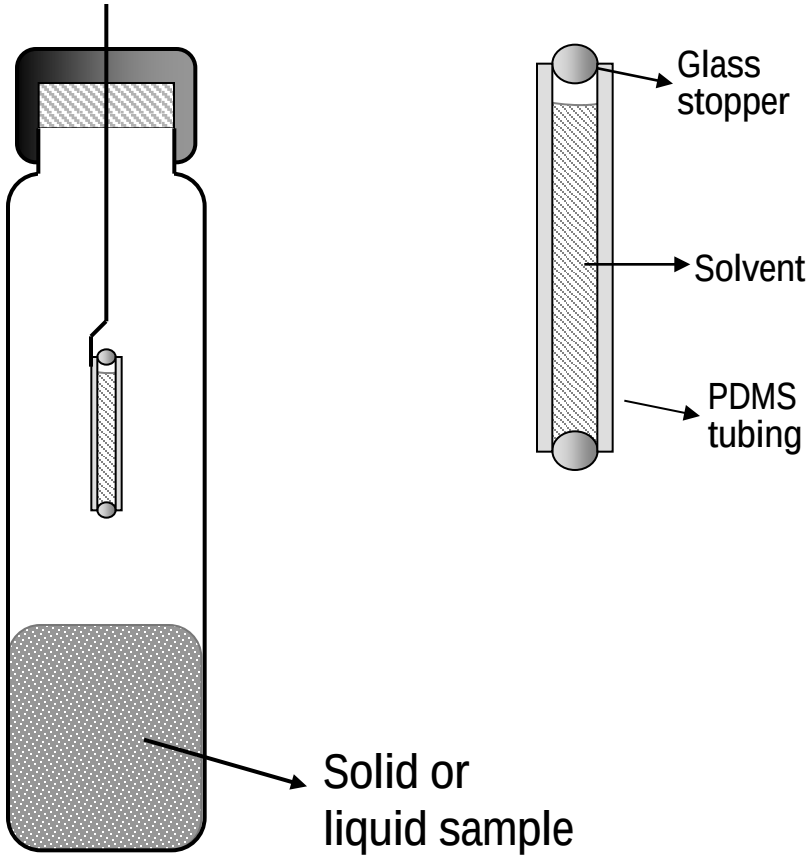


Figure 2

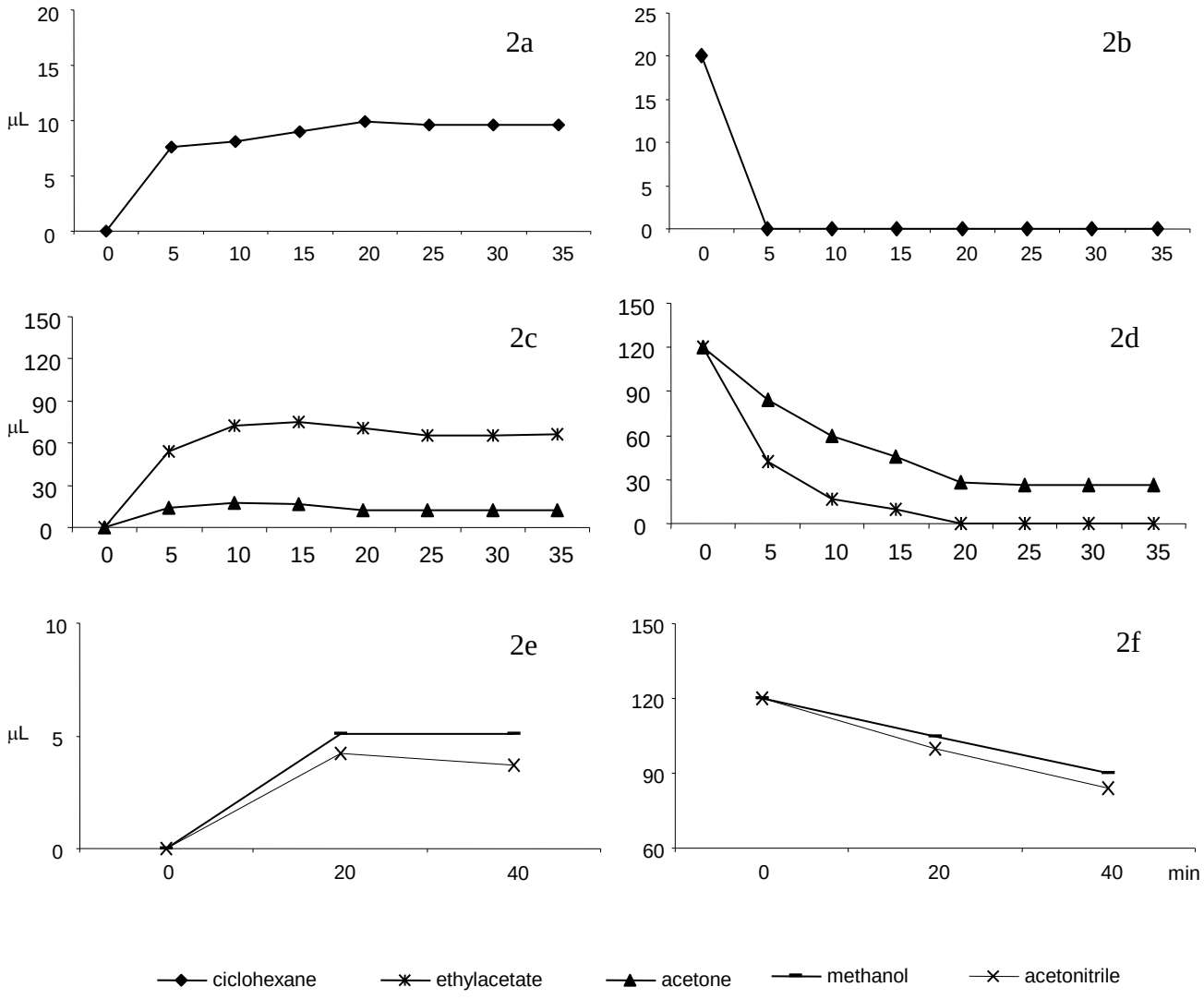

2a
2b
2c
2d
2e
2f
µL
min
ciclohexane
ethylacetate
acetone
methanol
acetonitrile

Figure 3

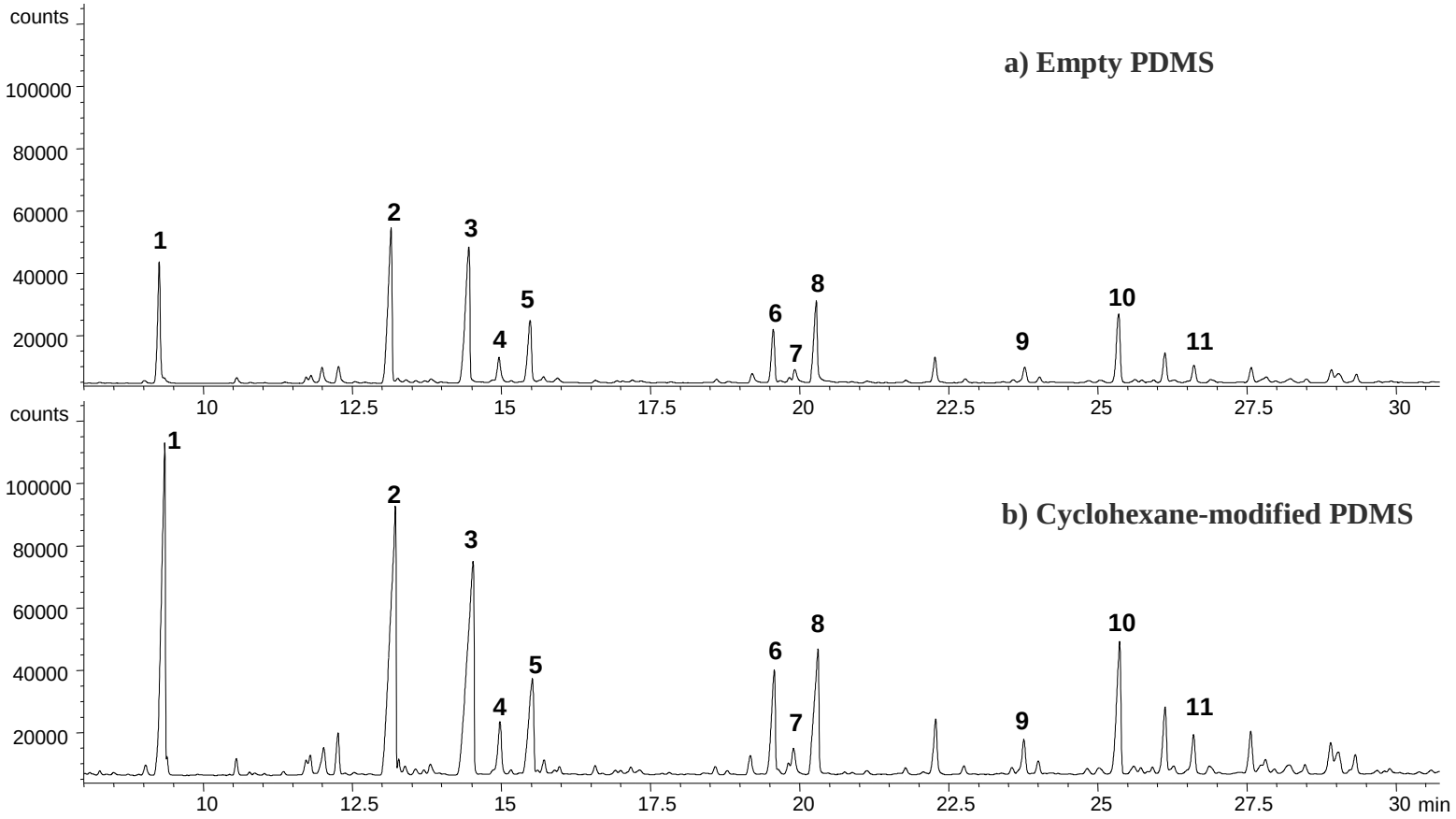

counts
100000
80000
60000
40000
20000
a) Empty PDMS
1
2
3
4
5
6
7
8
9
10
11
10
12.5
15
17.5
20
22.5
25
27.5
30
counts
100000
80000
60000
40000
20000
b) Cyclohexane-modified PDMS
1
2
3
4
5
6
7
8
9
10
11
10
12.5
15
17.5
20
22.5
25
27.5
30 min

Figure 4

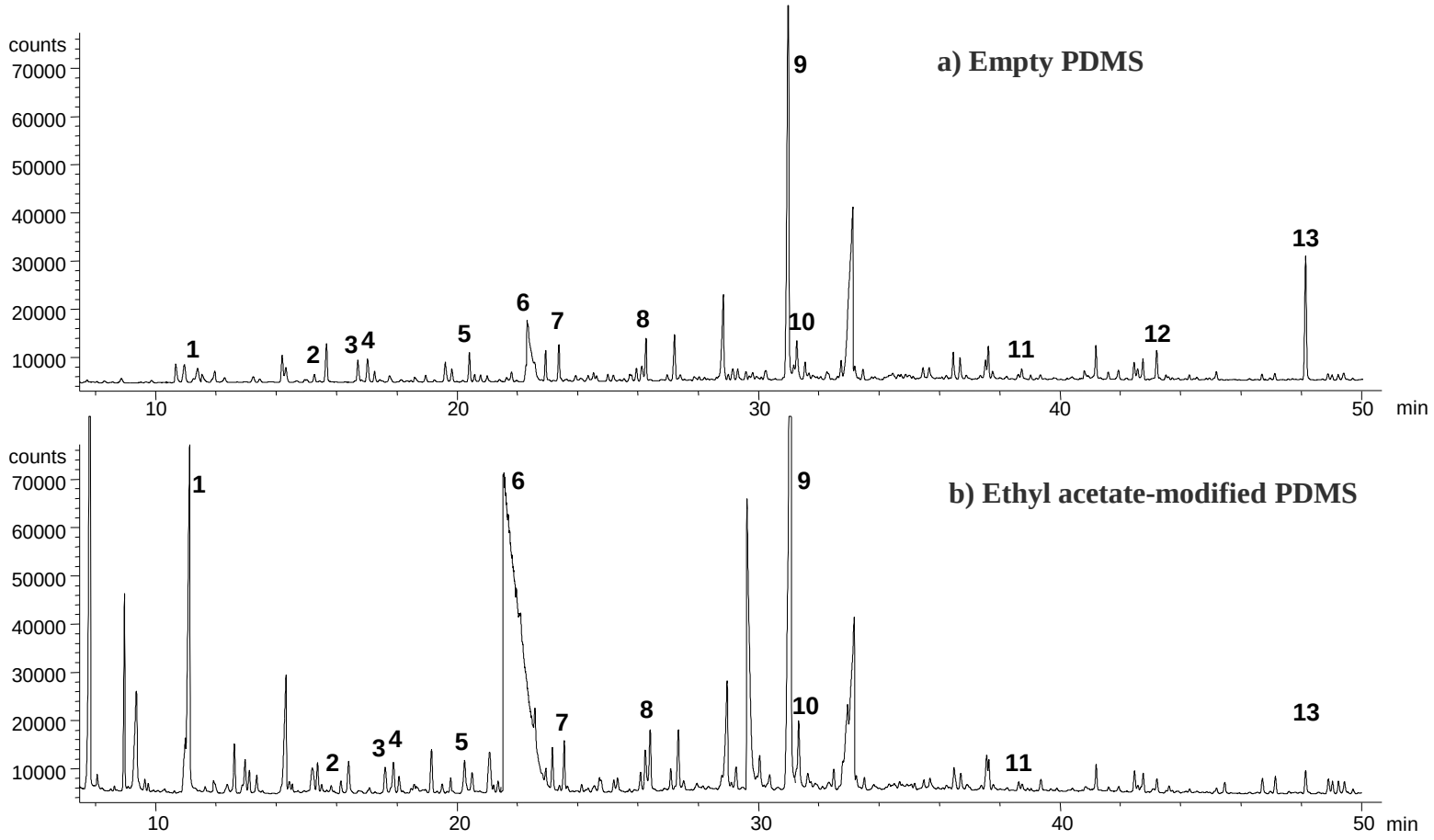
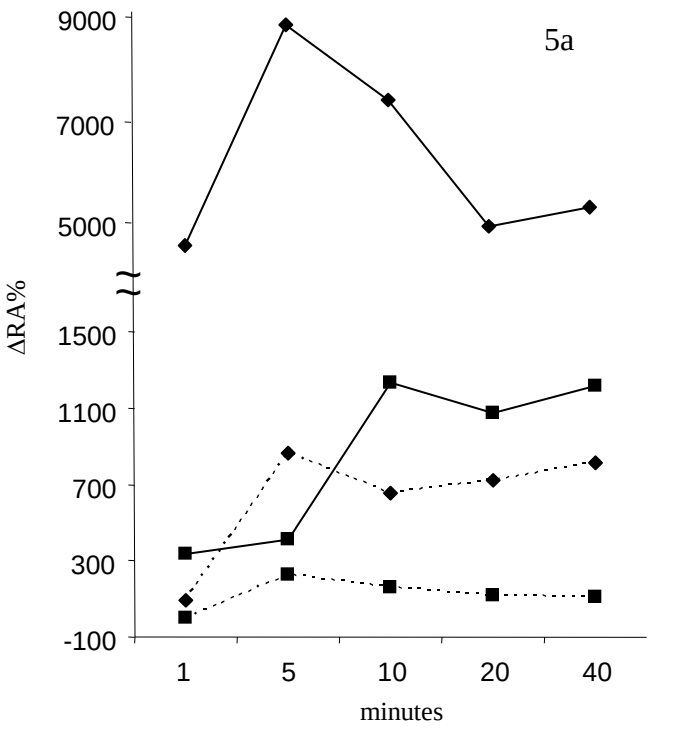
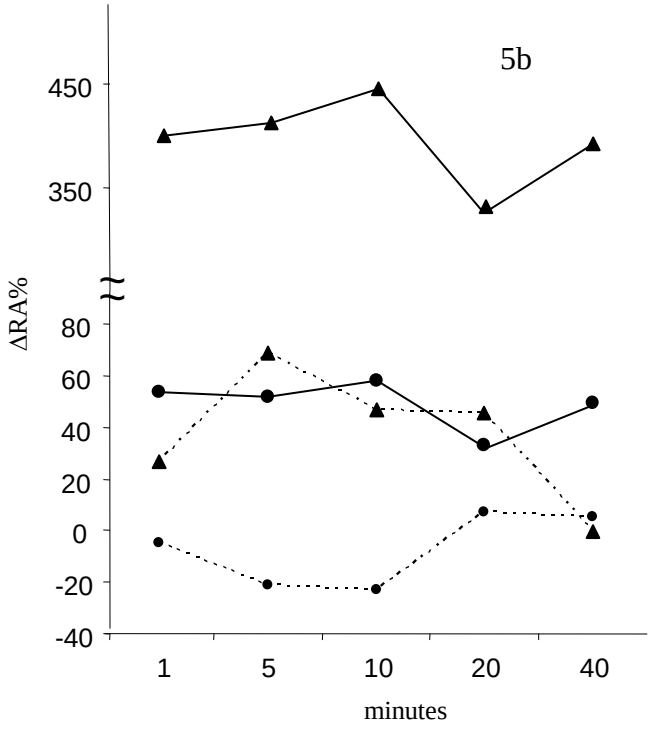
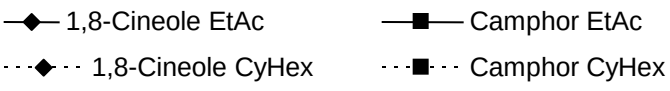
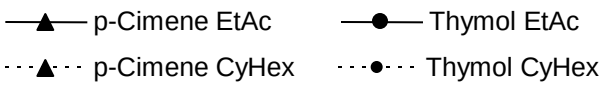

counts
70000
60000
50000
40000
30000
20000
10000
a) Empty PDMS
1
2
3
4
5
6
7
8
9
10
11
12
13
10
20
30
40
50
min
counts
70000
60000
50000
40000
30000
20000
10000
b) Ethyl acetate-modified PDMS
1
2
3
4
5
6
7
8
9
10
11
13
10
20
30
40
50
min

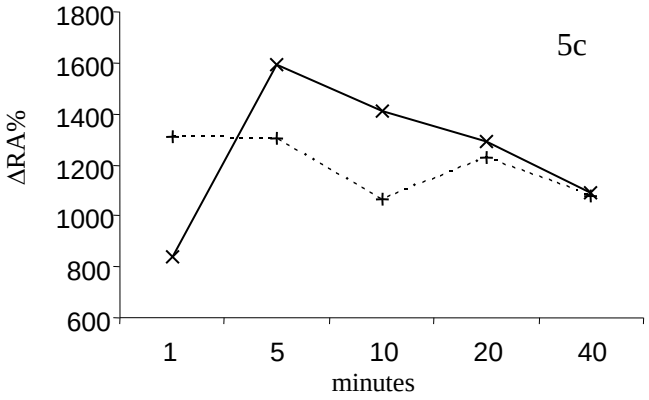
Figure 5

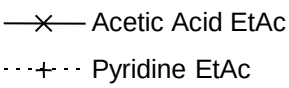

5a
9000
7000
5000
1500
1100
700
300
-100
ΔRA%
1
5
10
20
40
minutes


5b
450
350
80
60
40
20
0
-20
-40
ΔRA%
1
5
10
20
40
minutes


1,8-Cineole EtAc
Camphor EtAc
1,8-Cineole CyHex
Camphor CyHex


p-Cimene EtAc
Thymol EtAc
p-Cimene CyHex
Thymol CyHex


5c
1800
1600
1400
1200
1000
800
600
ΔRA%
1
5
10
20
40
minutes


Acetic Acid EtAc
Pyridine EtAc