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Headspace Sorptive Extraction (HSSE), Stir Bar Sorptive Extraction (SBSE), and Solid Phase Microextraction (SPME) Applied to the Analysis of Roasted Arabica Coffee and Coffee Brew

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Headspace sorptive extraction (HSSE) and stir bar sorptive extraction (SBSE), two recently introduced solventless enrichment techniques, have been applied to the analysis of the headspace of Arabica roasted coffee and of the headspace of the brew and of the brew itself. In both HSSE and SBSE enrichment is performed on a thick film of poly(dimethylsiloxane) (PDMS) coated onto a magnet incorporated in a glass jacket. Sampling is done by placing the PDMS stir bar in the headspace (gas phase extraction or HSSE) or by immersing it in the liquid (liquid phase extraction or SBSE). The stir bar is then thermally desorbed on-line with capillary GC-MS. The performance of HSSE and SBSE have been compared through the determination of the recoveries and relative abundances of 16 components of the coffee volatile fraction to classical static headspace (S-HS) and to headspace and in-sample solid phase microextraction (HS-SPME and IS-SPME, respectively) applying the fibers PDMS 100 μm, Carbowax/divinylbenzene 65 μm (CW/DVB), Carboxen/PDMS 75 μm (CAR/PDMS), polyacrylate 85 μm (PA), PDMS/divinylbenzene 65 μm (PDMS/DVB), and Carboxen/divinylbenzene/PDMS 50−30 μm (CAR/PDMS/DVB). In all cases, HSSE and SBSE gave higher recoveries, and this is entirely due to the high amount of PDMS applied.

KEYWORDS: Headspace sorptive extraction (HSSE); stir bar sorptive extraction (SBSE); static headspace (S-HS); solid phase microextraction (SPME); Arabica roasted coffee; coffee brew

INTRODUCTION

Several approaches for the sorptive extraction of analytes from gaseous and liquid matrices by means of poly(dimethylsiloxane) (PDMS) have been described. The principle of the different sorptive sampling methods and their applicability have been reviewed by Baltussen et al. (*1*). Sorptive extraction is defined as the partitioning of compounds in the two-phase system water (or headspace)/PDMS and is a bulk retention and not surface adsorption. A list of the abbreviations used in this paper and their meanings is given in **Table 1**.

One of us recently described a new sampling technique to extract organic analytes from aqueous samples by sorption onto a thick film (from 25 to 125 μL) of PDMS coated on a magnet incorporated in a glass jacket to avoid PDMS decomposition. The technique is named stir bar sorptive extraction (SBSE) (*1*), and the stir bars have been commercialized under the name Twister. The analytes are extracted by stirring the bar in the aqueous sample for a fixed time, recovered by desorbing the stir bar thermally either directly into a GC injector liner or into a glass tube inserted into a thermal desorption system, and then analyzed by capillary GC-FID or capillary GC-MS.

Table 1. Abbreviations and Their Meanings

abbreviation	definition
PDMS	poly(dimethylsiloxane)
SBSE	stir bar sorptive extraction
IS-SPME	in-sample solid phase microextraction
S-HS	static headspace sampling
D-HS	dynamic headspace sampling
SPME	solid phase microextraction
HS-SPME	headspace solid phase microextraction
HSSE	headspace sorptive extraction
RA	relative abundance
K_1	PDMS stir bar/sample headspace distribution coefficient
CF	concentration factor
PCA	principal component analysis
PDMS/DVB	PDMS/divinylbenzene fiber, 65 μm
CAR/PDMS	Carboxen/poly(dimethylsiloxane) fiber, 75 μm
PDMS 100	poly(dimethylsiloxane) fiber, 100 μm
CW/DVB	Carbowax/divinylbenzene fiber, 65 μm
PA	polyacrylate fiber, 85 μm
CAR/DVB/PDMS	Carboxen/divinylbenzene/PDMS fiber, 50–30 μm
V_f	volume of the SPME fiber coating material
TDS	thermo desorption system
CIS	cooled injection system
PTV	programmed temperature vaporizer

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The fundamental aspects of SBSE for liquid phase sampling are similar to the principles of in-sample solid phase microextraction (IS-SPME) because the two techniques are based on sorptive extraction (*1*). SBSE has shown to offer much higher recoveries than IS-SPME, thus overcoming one of its main limitations, namely, the low concentration capability due to the low volume of polymeric coating. In SPME the maximum volume of PDMS coated onto the fiber is 0.6 μL (100 μm fiber), whereas in SBSE it ranges from 25 to 125 μL.

Headspace samplings in the static (S−HS) or dynamic (D-HS) mode are solvent-free techniques widely used to analyze the volatile fraction of liquid and solid matrices. Headspace sampling can also successfully be achieved by SPME (HS-SPME) (*2*). This concentrating technique lies between S−HS and D-HS and is as reproducible and easy to automate as S-HS while giving enrichment factors as good as in D-HS. The HS-SPME concentration capability is significantly influenced by the fiber coating composition, as illustrated by Bicchi et al. (*3*) and Roberts et al. (*4*).

A previous paper described the use of PDMS stir bars in headspace sampling, the theory of headspace sorptive extraction (HSSE), and, besides environmental illustrations, some applications related to the analysis of flavors and fragrances (*5*). HSSE was applied to the aromatic and medicinal plants rosemary, sage, thyme, and valerian, and the results were compared to those obtained by SPME (*6*). The HSSE concentration capability was better than that obtained with HS-SPME with different fibers when evaluated through the relative abundance (RA) of some typical components of the plants investigated. The concentration capability of PDMS stir bars versus S-HS and HS−SPME with different fibers was also evaluated by determining the distribution coefficients between PDMS stir bar and sample headspace (K_1) and the concentration factors (CF) of a standard mixture of C_5−C_7 highly volatile compounds.

Several groups applied SPME to analyze coffee aroma and flavor. Among others, Hawthorne et al. (*7*) directly determined caffeine in coffee, tea, and carbonated beverages with quantitative reproducibility of ∼5%; Yang and Peppard (*8*) analyzed espresso-roast ground coffee by HS-SPME/GC; Wang et al. (*9*) described the determination of Veltol (2-methyl-3-hydroxy-4-pyrone) and Veltol Plus (2-ethyl-3-hydroxy-4-pyrone) in several matrices including coffee-based beverages, and Bicchi et al. (*10*) applied principal component analysis (PCA) to the SPME/GC patterns of either headspace or hot-water extract of roasted coffees of different origins or which had undergone different technological treatments or blends of different compositions. Deibler et al. (*11*) successfully applied SPME to the preparation of samples of brewed coffee for GC−olfactometry based on dilution analysis (Charm analysis). In a study aiming to evaluate the SPME fiber's ability to (ad)sorb flavor compounds under various conditions from coffee and aqueous flavored solutions, Roberts et al. (*4*) found that the poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB) coating had the highest overall sampling capability, whereas Carboxen/poly(dimethylsiloxane) (CAR/PDMS) was the most effective for small molecules and acids.

This contribution reports the results for HSSE applied to the roasted coffee and for HSSE and SBSE applied to the corresponding brews prepared in the Turkish mode of two Arabica coffee samples of different origin (Costa Rica and Guatemala). The data are compared with S-HS and with IS-SPME and HS-SPME using different fiber coatings.

EXPERIMENTAL PROCEDURES

Coffee Samples. Roasted Arabica coffee samples from Costa Rica and Guatemala were supplied by Lavazza SpA, Torino, Italy. Samples of 50 g were hermetically sealed under vacuum in nonpermeable polypropylene/aluminum/polyethylene packages and stored at −20 °C after roasting, until used for chemical analysis. All coffee samples were roasted for 6 min at 270 °C in a Probat laboratory roasting device (Emmerich).

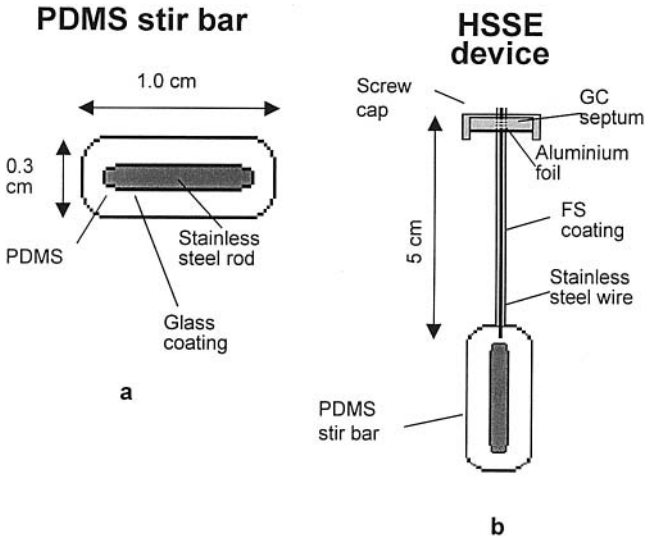

Figure 1. PDMS stir bar (a) and HSSE sampling device (b).

Table 2. Selected Components with Abbreviation and Peak Number

compound	abbrev	no.
2,3-pentanedione	PDO	**4**
pyrazine	PYR	**6**
2-methylpyrazine	MPY	**8**
2,6-dimethylpyrazine	DMP	**12**
3-ethyl-2,5-dimethylpyrazine	EMP	**20**
2-furancarboxyaldehyde	FCA	**21**
2-oxopropyl acetate	OPA	**22**
5-furfurylmethyl sulfide	FMS	**23**
2-acetylfuran	ACF	**24**
2-furanmethanolacetate	FMA	**28**
5-methylfurfural	MFA	**30**
N-methylpyrrol-2-aldehyde	MPA	**33**
2-furanmethanol	FMO	**36**
kahweofuran	KWF	**45**
pyrrole-1-furfurylmethyl isomer	PFM	**52**
2-acetylpyrrole	ACP	**54**

Coffee brews were prepared under strictly standardized conditions according to the so-called Turkish method. This procedure was chosen because it was the easiest to standardize. Thirty milliliters of boiling water was poured onto 6 g of roasted coffee in a 100 mL beaker. The mixture was again boiled for another 20 s under stirring, left for 9 min, and filtered under vacuum.

Sample Preparation. Each coffee package was left to reach ambient temperature before sampling. A series of experiments by S-HS were made to select the most suitable temperature and equilibration time to obtain a significant headspace profile.

One hundred and eighty milligrams of each roasted coffee was hermetically sealed in a 12.5 mL vial and equilibrated for 30 min in the thermostatic bath of the S-HS injector at 50 °C before injection. This temperature was also chosen because it is usually adopted for sensory tests.

Three milliliters of each coffee brew prepared as described above was transferred into a 12.5 mL vial. The vial was then hermetically sealed and equilibrated for 30 min at 50 °C under stirring in the thermostatic bath of the S-HS injector before injection. The same conditions were applied to HS-SPME and to HSSE to standardize the sample preparation procedure so that results could be compared.

Sampling. *Static Headspace (S-HS) Sampling.* A Carlo Erba HS-250 automatic HS injection system assembled on a Carlo Erba Mega 5360 GC (Thermoquest, Rodano, Italy) was used. One milliliter of the

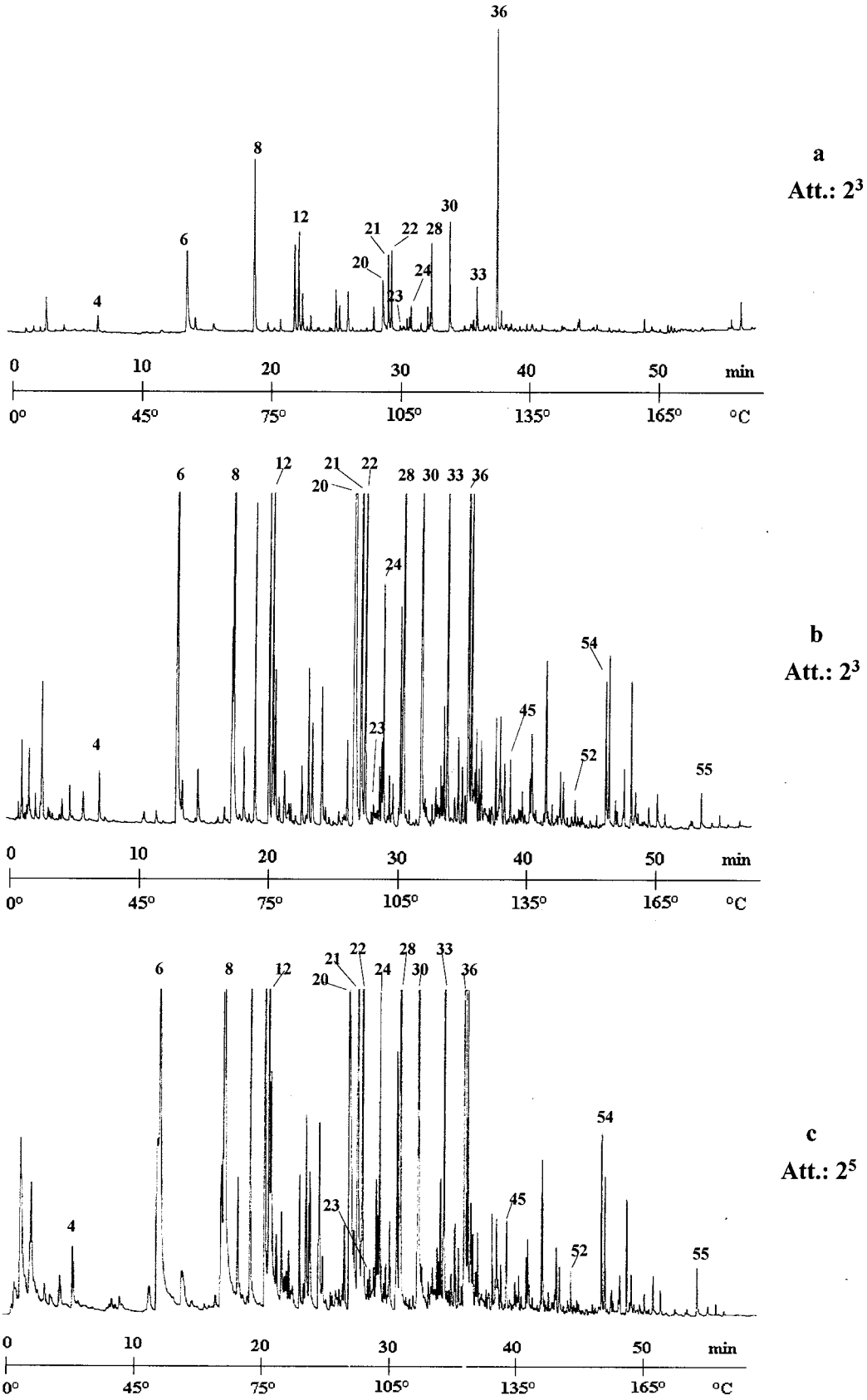

Figure 2. Capillary GC patterns of Costa Rican roasted coffee headspace after sampling by (a) HS-SPME with a PDMS 100 fiber (Att. 2^3), (b) HS-SPME with a CAR/DVB/PDMS fiber (Att. 2^3), and (c) HSSE with a PDMS bar (Att. 2^5).

vapor phase was directly injected into the GC system. Each experiment was repeated three times.

Headspace Solid Phase Microextraction (HS-SPME) Sampling. The SPME device and fibers were purchased from Supelco (Bellefonte, PA). The following fibers were used: poly(dimethylsiloxane) 100 μm [PDMS 100; volume of the coating material (V_f) = 0.612 mm^3]; Carbowax/divinylbenzene 65 μm [CW/DVB; V_f = 0.357 mm^3]; Carboxen/PDMS 75 μm [CAR/PDMS; V_f = 0.436 mm^3];

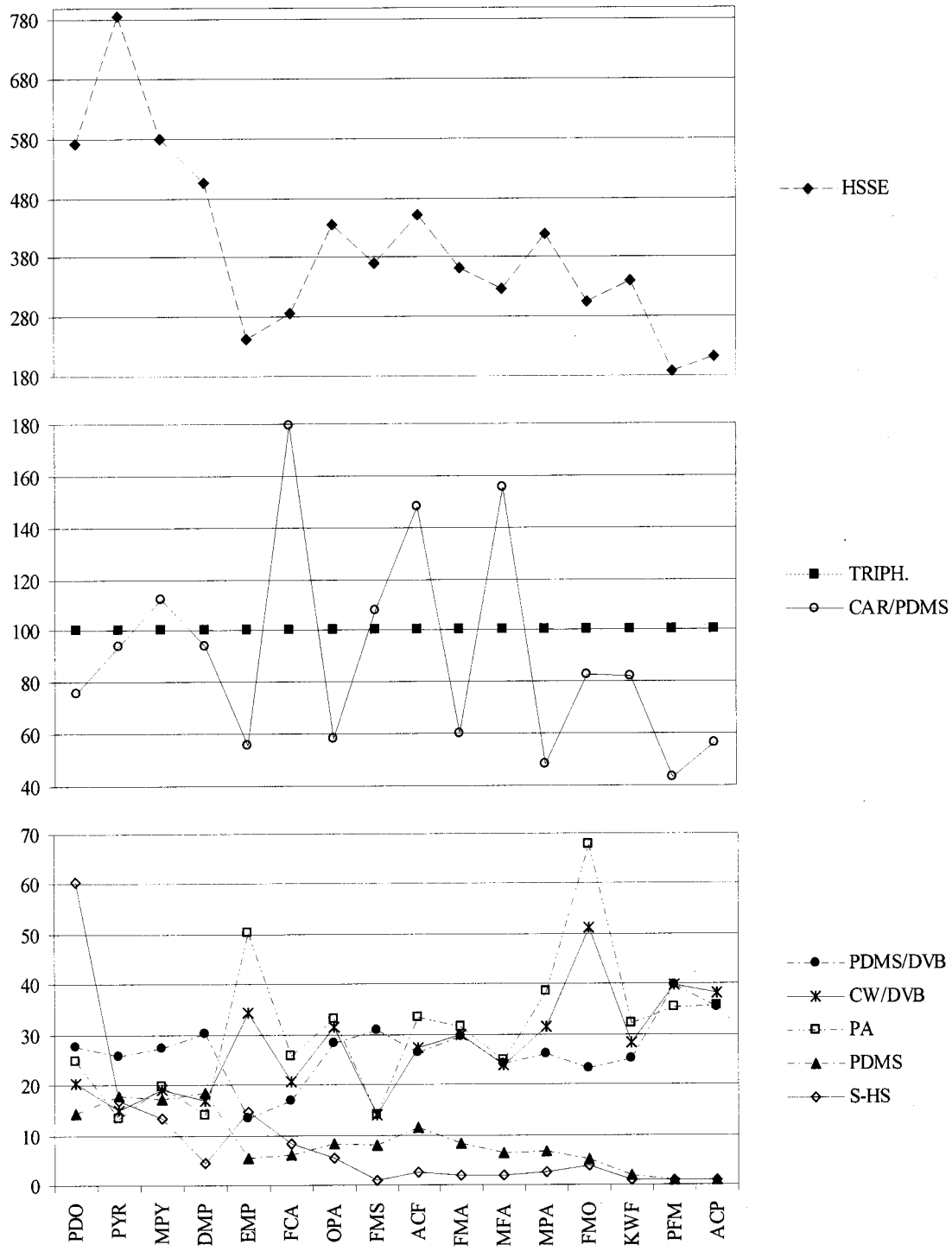

Figure 3. RAs of the Costa Rican coffee headspace components when analyzed by S-HS, HS-SPME with different fibers, and HSSE (for details see text). CAR/DVB/PDMS: TRIPH.

polyacrylate 85 μm [PA; V_f = 0.521 mm^3]; PDMS/divinylbenzene 65 μm [PDMS/DVB; V_f = 0.357 mm^3]; Carboxen/divinylbenzene/PDMS 50−30 μm [CAR/DVB/PDMS; V_f = 0.500 mm^3]. All fibers were conditioned before use as recommended by the manufacturer. The SPME device was inserted in the sealed vial containing the sample prepared as described above, and the fiber was exposed to the roasted coffee (or coffee brew) headspace for 30 min during HS equilibration (*12*). The vial was vibrated for 10 s every 10 min with an electric engraver (Vibro-Graver V74, Burgess Vibrocrafters Inc, Brayslake, IL) to speed the equilibration process of the analytes between the headspace phase and the fiber coating (*2*, *13*). Only that part of the vial in which the solid or liquid sample was present was thermostated in order to keep the SPME fiber as cool as possible to improve the vapor phase/fiber coating distribution coefficient (*14*). After sampling, the SPME device was immediately inserted into the GC injector for thermal desorption for 10 min at 230 °C. Before the next sampling, each fiber was reconditioned for 30 min in the GC injection port at 230 °C. Each experiment was carried out in triplicate.

In-Sample Solid Phase Microextraction (IS-SPME) Sampling. Each SPME fiber (see above) was plunged into the coffee brew (10 mL) and equilibrated for 30 min under stirring in the thermostatic bath of the S-HS injector at 50 °C. After extraction, the SPME device was removed from the sample, immediately inserted into the GC injector, and thermally desorbed at 230 °C for 10 min. Each experiment was repeated three times.

Headspace Sorptive Extraction (HSSE). PDMS stir bars with a volume of 55 μL were prepared as described (*1*). They are also available from Gerstel GmbH (Mülheim a/d Ruhr, Germany). Sampling was by suspending the stir bar (**Figure 1a**) with a wire in the headspace of the roasted coffee (180 mg) or of the coffee brew (3 mL) for 30 min. The stir bar was correctly positioned in the headspace volume by using a stainless steel wire (l = 5 cm; o.d. = 200 μm), one end of which was inserted into the PDMS coating while the other end was inserted through a GC septum (**Figure 1b**). To avoid adsorption, the septum was covered with aluminum paper and the wire enveloped in 0.25 mm i.d. fused silica tubing. The glass sampling vials were modified by replacing the top with a suitable screw thread so that they could be hermetically sealed with the GC injector screw cap. After sampling, the HSSE device was unscrewed from the headspace sampling vial and immediately screwed onto the GC injector through the injector screw cap. The PDMS stir bar was then thermally desorbed. New PDMS stir bars were conditioned for 4 h at 300 °C, whereas, between samplings, they were reconditioned for 20 min in the GC injection port at 230 °C to avoid "carry-over" effects. Each experiment was repeated three times.

Stir Bar Sorptive Extraction (SBSE). The PDMS stir bar (l = 1 cm; vol = 55 μL) was plunged into the coffee brew (10 mL) and equilibrated for 30 min under constant stirring in the thermostatic bath of the S-HS injector at 50 °C. After extraction, the PDMS stir bar was removed from the sample, dried with filter paper, and then inserted into the GC injector where the analytes were thermally recovered at 230 °C. Each experiment was repeated three times.

Instrumentation. *Capillary GC-FID Analysis.* Capillary GC-FID analyses were carried out on a Carlo Erba Mega 5360 GC unit. A FSOT poly(ethylene glycol) column (d_f = 0.5 μm, i.d. = 0.25 mm, l = 30 m) (CP-Wax 52 CB, Chrompack, Middelburg, The Netherlands) was used. Chromatographic conditions were as follows: injection system, splitless; injector temperature, 230 °C; temperature program, from 0 to 30 °C (5 min) at 40 °C/min and then to 250 °C (5 min) at 3 °C/min; detector, FID; temperature, 250 °C; carrier gas, hydrogen; flow rate, 1.5 mL/min.

Capillary GC-MS Analysis. Capillary GC-MS analyses in the electron impact mode were performed on an Agilent 6890 GC 5973N MS system (Agilent, Little Falls, DE) by applying the same column and conditions as for the GC-FID analyses. The inlet was operated in the splitless mode, and the carrier gas was helium. The HS components were identified by comparison of their mass spectra with those of authentic samples or with data from the literature.

Thermal desorption in HSSE and SBSE was done with a TDS-2 unit from Gerstel installed on the 6890 GC unit. For the TDS the following parameters were used: desorption program, from 20 °C at 30 °C/min to 280 °C (5 min); carrier gas, He; constant flow, 1 mL/min; flow mode, splitless; transfer line, 280 °C. A Gerstel CIS-4 PTV injector was used for cryogenic focusing of the analytes thermally desorbed from the stir bar. The PTV was cooled to −10 °C using liquid CO_2, with PTV in *sample remove* mode injection and injection temperature of −10 °C raised at 600 °C/min to 280 °C, 5 min.

RESULTS AND DISCUSSION

Sixteen coffee components with different structures, volatilities, and polarities characterizing both the headspace and the brew were chosen to compare the performances of the applied enrichment techniques (Table 2). Mean absolute area values were calculated by triplicate analysis for each experiment. Area variations for each component over the three experiments were always below 10%, that is, within the levels reported elsewhere (*1*, *5*, *6*). Moreover, PDMS stir bar reproducibility was evaluated by HSSE of Guatemalan roasted coffee and SBSE of the related brew with three new and preconditioned PDMS stir bars. The absolute area variations for the selected components were all below 10% for both techniques.

To make analytical data comparable, the peak areas of each selected component in all coffee samples were percent normalized by referring its peak area to that obtained by HS-SPME with the CAR/DVB/PDMS fiber taken as 100. This affords a relative abundance (RA) of each component obtained with each fiber or with the PDMS stir bar versus that of the CAR/DVB/PDMS fiber. This fiber was chosen because its three-component composition gives high recoveries for analytes with different structures and polarities (*3*, *4*).

Table 3. S-HS, HS-SPME, and HSSE RAs of the Components of the Guatemalan Roasted Coffee versus the CAR/PDMS/DVB (TRIPH) Fiber

		Guatemalan roasted coffee							
compound	no.	HSSE	TRIPH	CAR/ PDMS	PDMS/ DVB	CW/ DVB	PA	PDMS	S-HS
PDO	**4**	572	100	68	22	18	20	4	25
PYR	**6**	968	100	94	25	15	13	18	18
MPY	**8**	843	100	109	27	20	16	13	10
DMP	**12**	889	100	95	31	19	15	17	4
EMP	**20**	317	100	60	14	36	49	6	17
FCA	**21**	393	100	190	17	22	26	7	9
OPA	**22**	654	100	61	29	36	35	7	4
FMS	**23**	619	100	74	38	26	25	1	1
ACF	**24**	630	100	137	27	29	30	7	2
FMA	**28**	669	100	64	33	34	33	7	2
MFA	**30**	502	100	160	26	26	25	6	2
MPA	**33**	643	100	50	27	36	41	7	2
FMO	**36**	489	100	88	24	55	70	5	4
KWF	**45**	483	100	91	30	42	34	1	1
PFM	**52**	285	100	44	44	50	37	1	1
ACP	**54**	286	100	52	44	74	34	1	1

Table 4. S-HS, HS-SPME, and HSSE RAs of the Components of the Guatemalan Coffee Brew versus the CAR/PDMS/DVB (TRIPH) Fiber

		Guatemalan coffee brew							
compound	no.	HSSE	TRIPH	CAR/ PDMS	PDMS/ DVB	CW/ DVB	PA	PDMS	S-HS
PDO	**4**	320	100	257	26	30	8	8	1
PYR	**6**	1108	100	240	23	69	11	16	1
MPY	**8**	595	100	249	21	25	4	8	1
DMP	**12**	516	100	169	22	23	2	4	1
EMP	**20**	171	100	67	7	66	1	1	1
FCA	**21**	210	100	271	13	19	11	3	1
OPA	**22**	526	100	176	41	62	21	1	1
FMS	**23**	157	100	134	38	16	1	1	1
ACF	**24**	318	100	226	22	25	12	2	1
FMA	**28**	217	100	120	36	22	9	4	1
MFA	**30**	239	100	163	23	21	10	3	1
MPA	**33**	238	100	73	22	33	9	2	1
FMO	**36**	221	100	185	21	62	37	6	1
KWF	**45**	199	100	79	3	1	1	1	1
PFM	**52**	144	100	29	54	7	1	1	1
ACP	**54**	305	100	11	40	4	1	1	1

HS-SPME and HSSE Analyses of Roasted Coffee. Figure 2 shows the Costa Rican roasted coffee capillary GC patterns of (a) HS-SPME with the PDMS 100 fiber, (b) HS-SPME with the CAR/DVB/PDMS fiber, and (c) HSSE with a PDMS stir bar. **Figure 3** graphically visualizes the performances of the above sampling techniques for the Costa Rican roasted coffee headspace components in terms of their RAs. **Table 3** compares the RA data for S-HS, HS-SPME on the different fibers, and HSSE for the selected components of the Guatemalan roasted coffee samples. For both roasted coffees, PDMS stir bars always showed higher concentration capability than the SPME fibers applied. Stir bar recoveries are between 20 and 80 times higher compared to those from the HS-SPME PDMS fiber, which is entirely due to the higher volume of PDMS coating (55 vs 0.6 μL). As expected (*3*, *4*), in HS-SPME polar and multicomponent fibers were more effective than PDMS 100. In particular,

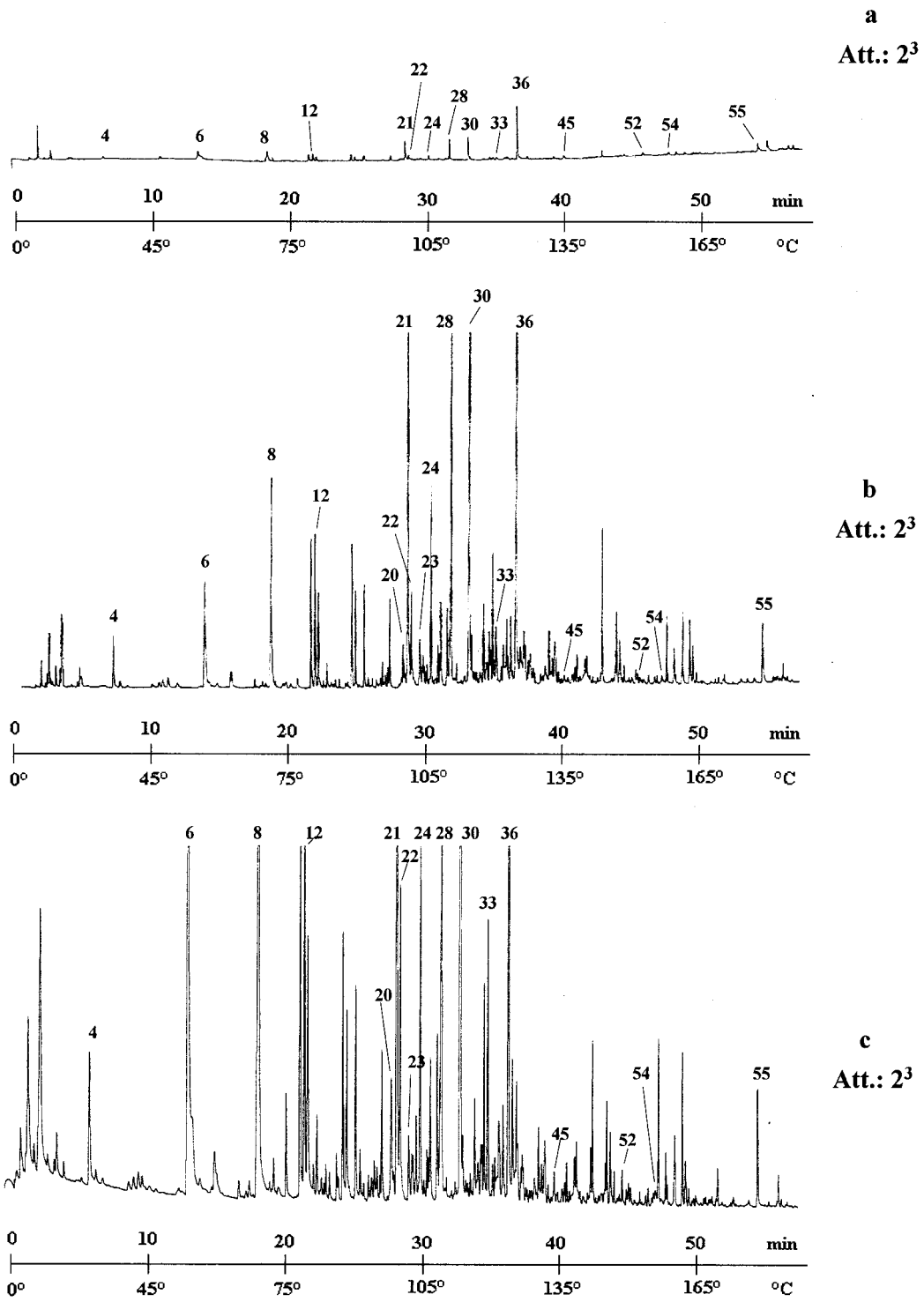

Figure 4. Capillary GC patterns of Costa Rican coffee brew headspace after sampling by (a) HS-SPME with a PDMS 100 fiber (Att. 2^3), (b) HS-SPME with a CAR/DVB/PDMS fiber (Att. 2^3), and (c) HSSE with a PDMS bar (Att. 2^3).

Carboxen-containing fibers gave high recoveries for some of the analytes [furancarboxaldehyde (*21*), 2-acetylfuran (*24*), and methylfurfural (*30*)]. Recoveries with fibers containing DVB or with PA are much lower. Classical static headspace (S-HS) exhibits the lowest sensitivity and, moreover, strong differences in vapor phase composition are noted.

HS-SPME and HSSE Analyses of Coffee Brews. Figure 4 shows the Costa Rican coffee brew GC patterns of (a) HS-SPME with the PDMS 100 fiber, (b) HS-SPME with the CAR/DVB/PDMS fiber, and (c) HSSE with a PDMS stir bar. **Figure 5** graphically represents the RAs of the Costa Rican coffee brew components. **Table 4** reports the RAs of the selected components of the Guatemalan coffee brew after S-HS, HS-SPME on the different fibers and HSSE sampling. In this case, too, the PDMS stir bar showed the best concentration capability, although RAs were somewhat lower than those obtained with roasted coffees. Both Costa Rican and Guatemalan coffee brew S-HS and HS-SPME-PDMS profiles were not significant. The highest concentration capability in HS-SPME was again achieved on the Carboxen/PDMS fiber, which gave recoveries for several components comparable to those of PDMS stir bars. From these experiments it is clear that adsorption rather than sorption is

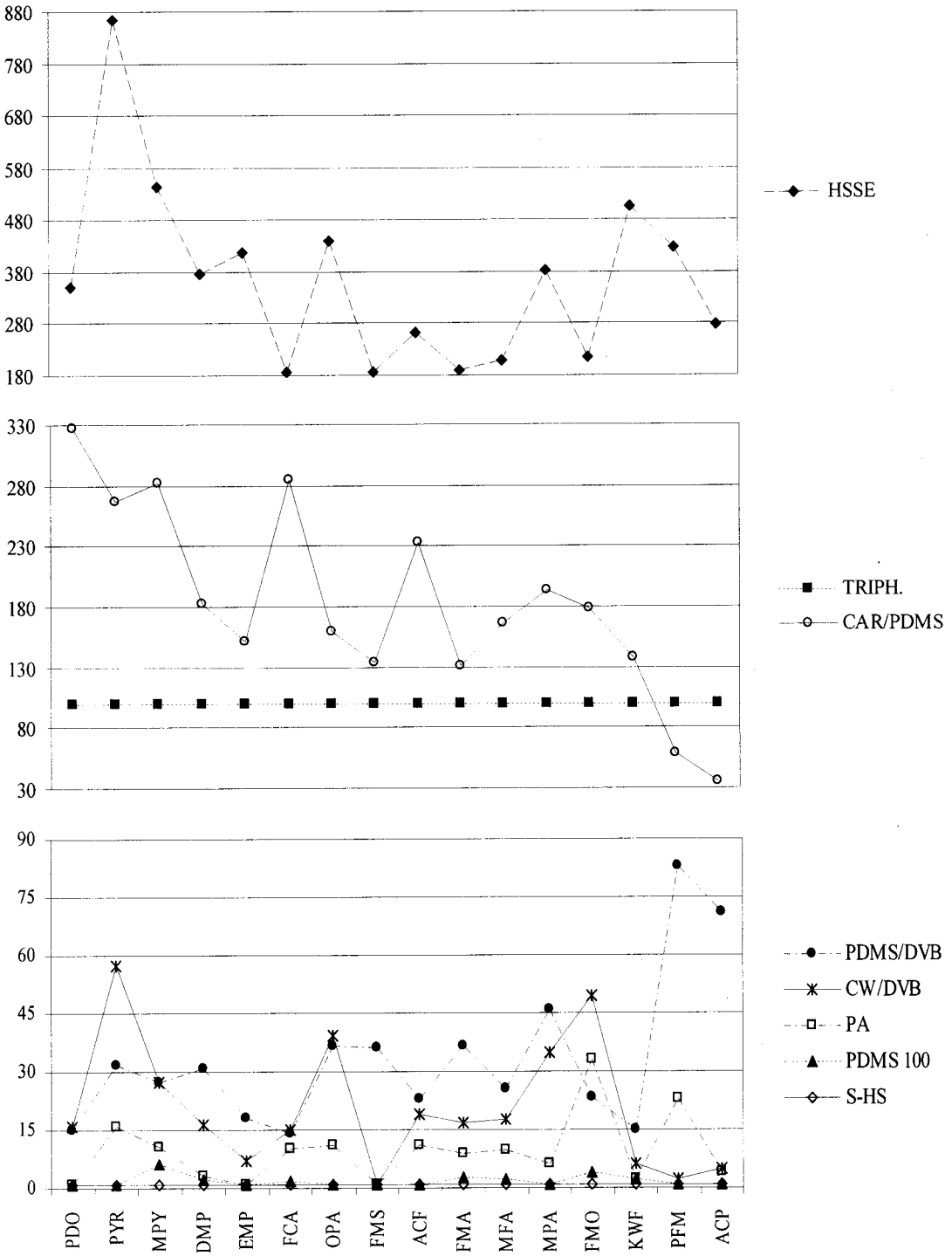

Figure 5. RAs of the Costa Rican coffee brew headspace components when analyzed by S-HS, HS-SPME with different fibers, and HSSE (for details see text). CAR/DVB/PDMS: TRIPH.

the operating mechanism in concentrating the analytes in HS-SPME because (a) the recoveries achieved with the PDMS fiber are very low and (b) the significantly different RA ratios of some of the components investigated [in particular 2,3-pentandione (*2*), pyrazine (*4*), and 2-methylpyrazine (*8*)] between roasted coffee and brew. These differences are especially evident with the CAR/DVB/PDMS and CAR/PDMS fibers and are probably due to the different headspace compositions and in particular to the significant vapor amounts contained in the brew headspace (*4*) and to the different behaviors of the fiber components as a consequence of the different headspace composition. The absolute areas of the brew HS components with CAR/DVB/PDMS are all significantly lower than those obtained with CAR/PDMS.

IS-SPME and SBSE Analyses of Coffee Brew. Figure 6 shows the Costa Rican coffee brew GC patterns of (a) IS-SPME with the PDMS 100 fiber, (b) IS-SPME with the CAR/DVB/PDMS fiber, and (c) SBSE with a PDMS stir bar. The RAs of the Costa Rican coffee brew components are graphically represented in **Figure 7**. **Table 5** reports the RAs of the selected components of the Guatemalan coffee brew after SBSE and IS-SPME samplings.

SBSE is by far the most effective technique to enrich the coffee brew characterizing components. Recoveries are generally

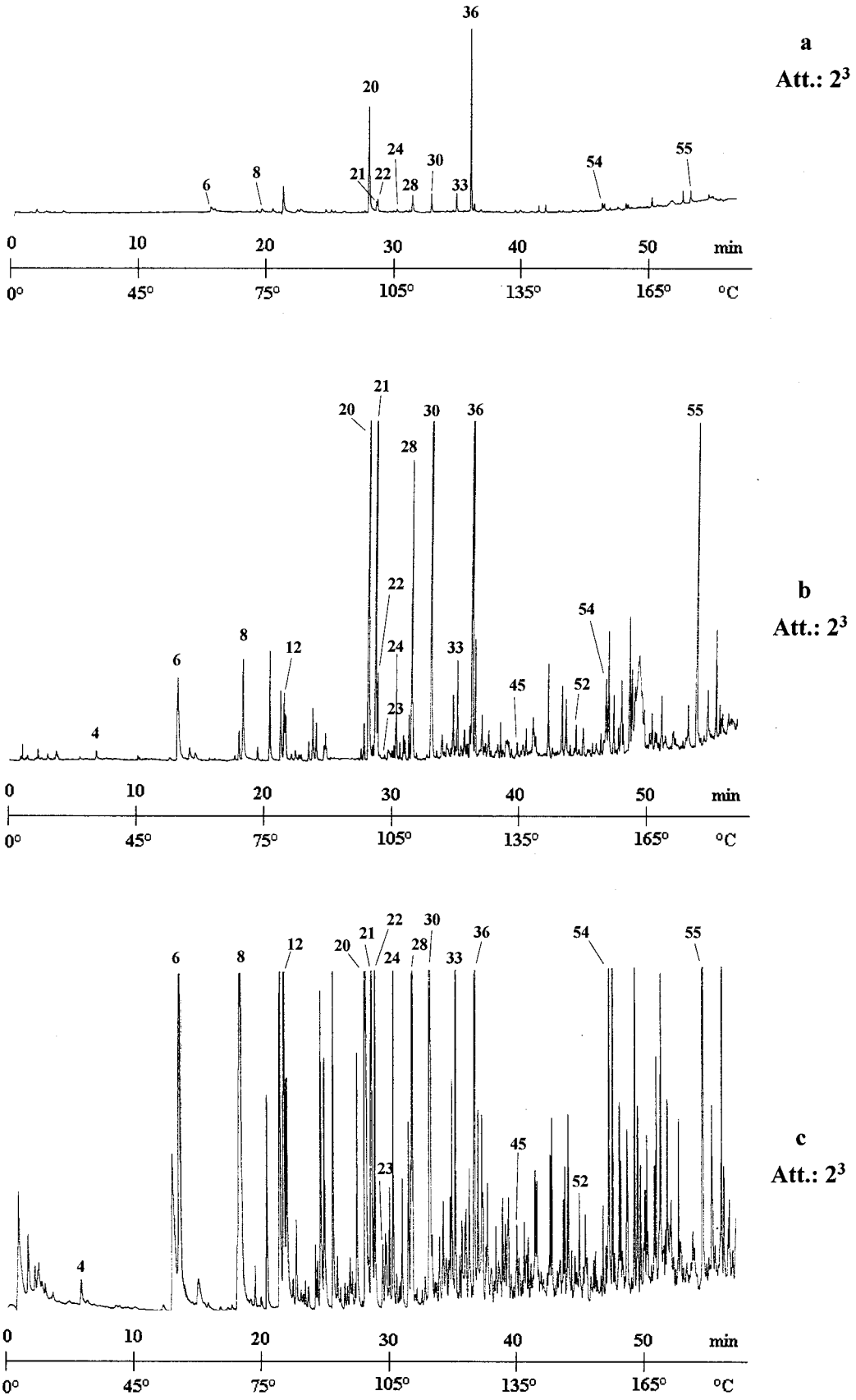

Figure 6. Capillary GC patterns of Costa Rican coffee brew after sampling by (a) IS-SPME with a PDMS 100 fiber (Att. 2^3), (b) IS-SPME with a CAR/DVB/PDMS fiber (Att. 2^3), and (c) SBSE with a PDMS bar (Att. 2^3).

1 order of magnitude higher than those obtained by IS-SPME with all fibers investigated. Significant signals were obtained only with the fibers containing Carboxen (i.e., CAR/DVB/PDMS and CAR/PDMS), whereas the other fibers (in particular, PDMS and PA) were not effective at all. The extremely high *RAs* of 5-furfurylmethyl sulfide (*23*) obtained with PDMS stir

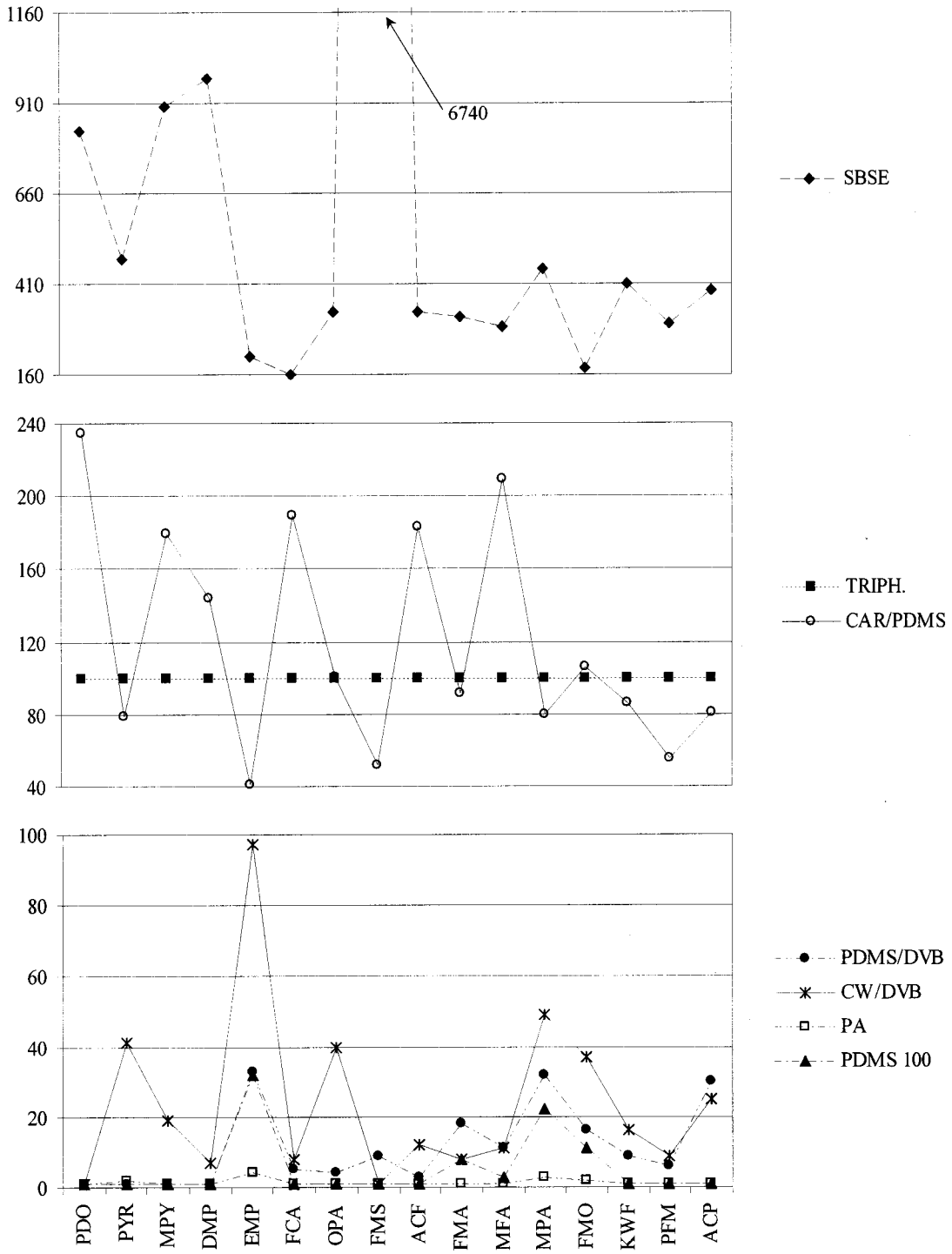

Figure 7. RAs of the Costa Rican coffee brew components when analyzed by IS-SPME with different fibers and SBSE (for details see text). CAR/DVB/PDMS: TRIPH.

bars must be attributed to its very low recovery with the reference CAR/DVB/PDMS fiber. It is known that sulfur compounds are strongly affected by the catalytic activity of carbon-based materials such as Carboxen (*15*).

From the above data, it can be concluded that HSSE and SBSE applying PDMS are the most powerful enrichment techniques. The repeatibility of HSSE and SBSE was evaluated through five consecutive series of samplings of roasted Guatemalan coffee and brew with the same stir bar. Although the stir bar drastically darkened, the area variability of the recovered characterizing components in both HSSE and SBSE experiments did not exceed 10% over the five series of analyses. One of the advantages of PDMS stir bars is that they can be used indifferently for SBSE or HSSE without affecting sampling effectiveness, thus affording correlation between the composition of the headspace and of the brew, in particular between those components with different volatilities characterizing the matrix organoleptic characteristics (e.g., smell and taste). **Figure 8** shows the areas of the investigated components after HSSE of the Guatemalan roasted coffee and brew and after SBSE of the coffee brew obtained with the same stir bar and illustrates how brew headspace and brew are correlated. Different volumes of coffee brew were used for HSSE and HS-SPME (3 mL) and for SBSE and IS-SPME (10 mL) samplings to obtain significant

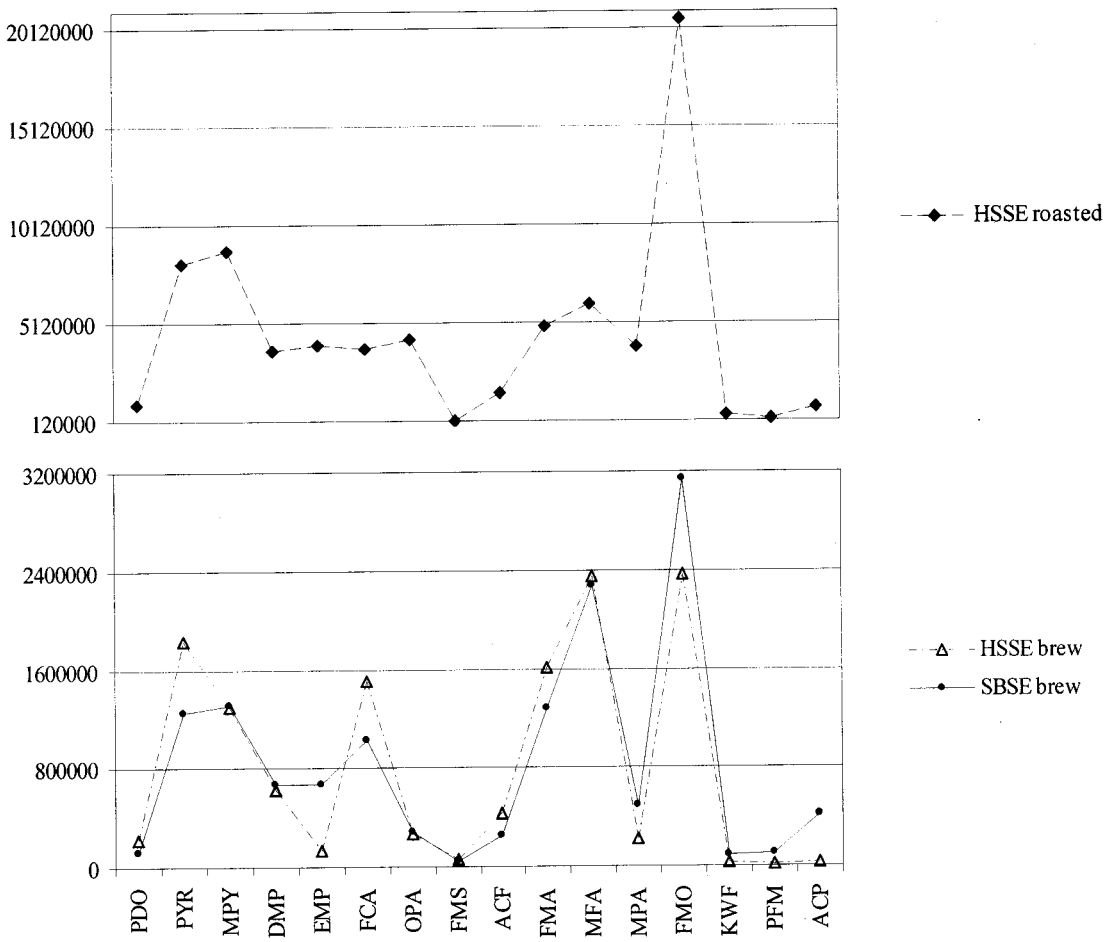

Figure 8. Areas of the investigated components after HSSE of the Guatemalan roasted coffee and brew (3 mL) and SBSE of the coffee brew (10 mL) obtained with the same stir bar.

Table 5. IS-SPME and SBSE RAs of the Components of the Guatemalan Coffee Brew versus the CAR/PDMS/DVB (TRIPH) Fiber

		Guatemalan coffe brew (in the sample)						
compound	no.	SBSE	TRIPH	PDMS/ DVB	CAR/ PDMS	CW/ DVB	PA	PDMS 100
PDO	**4**	1981	100	1	491	1	1	1
PYR	**6**	1574	100	54	115	1	1	1
MPY	**8**	1626	100	2	244	1	1	1
DMP	**12**	1610	100	2	141	62	1	1
EMP	**20**	185	100	48	88	46	1	1
FCA	**21**	314	100	9	300	8	2	18
OPA	**22**	471	100	8	103	5	1	1
FMS	**23**	3704	100	5	24	2	1	1
ACF	**24**	459	100	7	236	7	1	1
FMA	**28**	882	100	34	124	25	3	11
MFA	**30**	556	100	16	268	13	1	3
MPA	**33**	626	100	38	91	34	1	2
FMO	**36**	291	100	25	134	23	2	5
KWF	**45**	496	100	4	107	24	1	1
PFM	**52**	375	100	4	320	7	1	1
ACP	**54**	510	100	25	104	36	1	1

IS-SPME-GC profiles. Further studies on this topic are under way.

The higher recoveries obtained with PDMS stir bars compared to those with the SPME-PDMS fiber are solely due to the higher volume of polymeric coating. Both systems operate in the sorption mode, and enrichment is controlled by the water (or vapor)/PDMS partitioning constants of the analytes. The phase ratio β between water (or vapor) and PDMS is the controlling parameter in this enrichment mechanism (*1*). On the other hand, several authors (*3*, *4* and references therein) observed that the most effective SPME fibers giving simultaneously high recovery of apolar and polar analytes, were those containing PDMS (operating in the sorption mode) with one or two other components (DVB or Carboxen), mainly operating in adsorption mode. This phenomenon mainly depends on the physical characteristics of the surface of the adsorbent, on its specific interaction with each analyte, and on the competitive mutual interactions between the analytes and the adsorbent. HSSE and SBSE generally give good recoveries whatever the nature of the compounds and, although PDMS is a relatively low-polarity polymer, it discriminates less than SPME analytes with different structures and polarities sampled from a complex matrix or the same analytes sampled from different matrices [e.g., in particular, 2,3-pentandione (*2*), pyrazine (*4*), and 2-methylpyrazine (*8*) in roasted coffee and brew (**Figures 3** and **5**)]. The adsorption mechanism is difficult to control, and besides activity also displacement effect occurs. During this study of 10 CAR/DVB/PDMS fibers only 5 were performed in a highly reproducible way (RSD below 10%). On the other hand, all material based on sorption was highly reproducible.

In conclusion, the recently introduced HSSE and SBSE with PDMS stir bars have been successfully applied for the analysis of the headspace of roasted coffee and brew and for sampling of coffee brew. Both techniques are simple and easy to automate and do not require any preliminary sample preparation step while avoiding the use of toxic or environmentally unfriendly solvents.

PDMS stir bars showed better concentration capability than all SPME fibers. Moreover, the same principle can be applied to the analysis of headspace and liquid, providing new insight into the vapor/liquid phase distribution of aroma and flavor compounds.

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