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Dual-phase twisters: A new approach to headspace sorptive extraction and stir bar sorptive extraction

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Abstract

The fields of applicability of headspace sorptive extraction (HSSE) and stir bar sorptive extraction (SBSE) using polydimethylsiloxane (PDMS) as sorbent have been intensively discussed and widely described. One of the limits of sorptive extraction is that PDMS (i.e. an apolar phase) is the only polymer currently in use making it difficult to recover polar analytes from complex or multi-ingredient matrices and those with very volatile components (C1–C4 analytes). Dual-phase twisters are here introduced as new tools for HSSE and SBSE to overcome the above limits. Dual-phase twisters combine the concentration capabilities of two or more sampling materials operating in different ways (in this case sorption and adsorption). The new twisters consist of a short PDMS tube the ends of which are closed with two magnetic stoppers, thus creating an inner cavity that can be packed with different types of adsorbents like activated carbons. The concentration capability of dual-phase twisters was evaluated by using them for the HSSE and SBSE sampling of a number of matrices in the vegetable, food and environmental fields. The contributions made by different carbons to recovery, repeatability and intermediate precision were also investigated.

Keywords: HSSE; SBSE; Dual-phase twisters; Carbons; Sorption–adsorption

1. Introduction

Stir bar sorptive extraction (SBSE) is a high concentration capability solventless sample preparation technique first introduced by Sandra's group [1] to extract organic analytes from aqueous samples. Sorptive extraction was almost contemporarily applied to headspace sampling by Tienpont et al. [2] and Bicchi et al. [3], under the name of headspace sorptive extraction (HSSE). It is based on the sorption of an analyte(s) onto a thick film of polydimethylsiloxane (PDMS) coated on the magnet of a stir bar incorporated into a glass jacket. Analytes are sampled by introducing the PDMS stir bar directly into the liquid sample or suspending it in the matrix headspace for a fixed time. After sampling analytes are recovered from the PDMS by thermal desorption and on-line analyzed by cGC or cGC–MS. PDMS stir bars are marketed under the name Twister (Gerstel, Mülheim a/d Ruhr, Germany). Both SBSE and HSSE have been shown to be very useful in recovering trace components from liquid samples. SBSE has mainly and successfully been applied to the analysis of contaminants in several matrices, including, among others, organic pollutants [4–6], endocrine disrupters and estrogens [7–10] and organotin compounds [11,12] in water, odorants and off-flavours [13,14] and pesticide residue [15] in water and in food matrices [16–22], pharmaceuticals [23] and drugs of abuse [24] in biological fluids. On the other hand, HSSE has been applied to headspace sampling of several matrices including aromatic and medicinal plants [3], chiral monoterpenes in essential oils in combination with enantio-MDGC–MS [25], coffee [26], volatile fraction of French olive oil [27] and in the detection of volatile metabolites from toxigenic fungi [28,29].

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One of the limits of sorptive extraction is that PDMS (i.e. an apolar phase) is the only polymer at present adopted as a coating for stir bars. Recovery of polar analytes (i.e. with low $K_{o/w}$) is so poor that ultra-trace analysis of those analytes in complex or multi-ingredients matrices is problematic. Often in situ derivatization is applied for polar solutes to increase the log P values [24]. Stir bars coated with materials with a better affinity to polar compounds would improve SBSE flexibility and selectivity while maintaining (or even increasing) its concentration capability. New stir bars would also be very useful in HSSE, in particular, to sample very volatile components (C1–C4 analytes). These compounds are frequently discriminated in sorption processes since they are released from PDMS to the vapour phase because of their headspace/PDMS stir bar partition equilibriums and coefficients. Moreover, polymeric phases that can increase the sampling speed of ultratraces are also needed, in particular, when headspace composition is used as a parameter to monitor the dynamics and/or kinetics of biological processes. New approaches or concentrating materials are therefore required to overcome the above-mentioned limits of twisters and to extend the range of applications of sorptive extraction. One of the solutions is combining two or more sampling materials with concentration capabilities based on different principles in order to obtain a positive synergistic effect. A new generation of twisters exploiting sorption and adsorption simultaneously is introduced here: they consist of a short PDMS tube closed at both ends with two magnets, whose inner volume is packed with an adsorbent. In this study, different types of activated carbons have been used as packing material. Stir bars based on the above approach have been called *dual-phase twisters* to distinguish them from the conventional ones. The article reports the preliminary results achieved with dual-phase twisters using different carbons as a packing material, applied to the SBSE and HSSE sampling of a number of matrices in the vegetable, food and environmental fields.

2. Experimental

2.1. Materials and reagents

Homogeneous samples of dried sage leaves (*Salvia officinalis* L.) were from the University of Turin Botanical Garden. Coffee samples were 100% Arabica originating from Costa Rica. A commercially available wiskey and 1 ppb atrazine spiked water sample were also analyzed. Solvents were all pesticide-grade from Riedel-de Haen (Seelze Germany). Four carbons with different properties were used to prepare dual-phase twisters in particular: carbon RR (Carbopack B, code no. 20273), carbon RB (Carbopack C, code no. 10257), carbon BB (Carbosieve G, code no. 10198) and carbon BY (Carboxen 1000, code no. 10478-U). Carbons were purchased from Supelco (Bellefonte, PA, USA). Their characteristics are described in the Supelco catalogue.

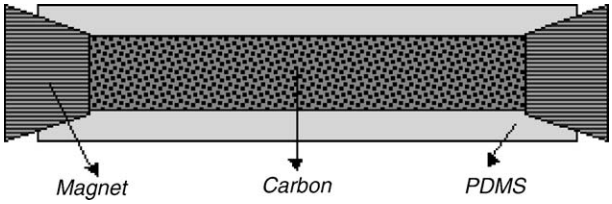

Fig. 1. Diagram of the dual-phase stir bar.

2.2. PDMS/carbon dual-phase twister

Differently polymerised PDMS tubes 0.5 and 1 mm thick, respectively, were used (Nalgene, Rochester, NY, USA). The tube (1 cm) is filled with 20 mg carbon material (Supelco, see above) and sealed on each side with a small (2 mm long) teflon-coated magnetic stir bar (Cole-palmer Instrument Co., Vernon Hills, IL, USA). A diagram of the dual-phase stir bar is reported in Fig. 1. The dual-phase stir bars are commercially available (Gerstel, Mulheim a/d Ruhr, Germany) (EU patent 05010432.2).

2.3. Sample preparation

2.3.1. Coffee and sage HSSE sampling

A first series of experiments was carried out with a set of seven twisters consisting of a conventional stir bar (PDMS volume: 20 μL, *l*: 1 cm, thickness: 0.5 mm), an empty dual-phase twister (PDMS volume: 20 μL, *l*: 1 cm, tube thickness: 0.5 mm), and four dual-phase twisters prepared with the same PDMS tube as above and packed with the above four carbons. A further series of experiments was carried out with a second set of twisters analogous to the previous ones except that for dual-phase twisters a tube 1 cm long and 1.0 mm thick was used resulting in a double PDMS volume (40 μL).

Fifty milligrams of powdered roasted Costa Rica coffee in a 250 mL Erlenmeyer flask was submitted to HSSE sampling with each twisters for 1 h at 50 °C. Sage leaves were sampled under the same conditions except that sample size was reduced to 5 mg to avoid cGC column overloading. Each matrix was analyzed three times with each stir bar. Blank runs were done with each stir bar before and after each analysis and no memory effects were observed.

2.3.1.1. Sampling procedure. Each twister was suspended into the vapour phase in equilibrium with the matrix and the headspace was sampled by HSSE under the conditions reported above. The twister was kept correctly positioned in the headspace volume by using an appropriate length of harmonic stainless steel wire, one end of which clamped the PDMS coating, while the other end was inserted into the flask septum stopper. After sampling, the twister was removed from the vapour phase, inserted into a glass tube and then introduced into a thermodesorber (TDU, Gerstel, Mülheim a/d Ruhr, Germany), for cGC–MS analysis (see Section 2.3). Each experiment was repeated three times.

2.3.1.2. Repeatability. The same sample of roasted Costa Rica coffee (50 mg) in a 250 mL Erlenmeyer flask was submitted to HSSE with a PDMS 0.5 mm/RR carbon dual-phase twister and then submitted to TDU-cGC–MS analysis. This analysis was repeated six times.

2.3.1.3. Intermediate precision. The same sample of roasted Costa Rica coffee (50 mg) in a 250 mL Erlenmeyer flask was submitted to HSSE with each of the five 1 mm PDMS/RR carbon dual-phase twister and then submitted to TDU-cGC–MS analysis. Three experiments were carried out for each dual-phase twister.

2.3.2. SBSE sampling

A commercially available whiskey sample diluted 10-fold with water (1 mL + 9 mL water) and a 1 ppb atrazine standard solution were submitted to SBSE with a conventional 1 cm × 0.5 mm PDMS stir bar and a 20 μL BB Carbon/PDMS dual-phase twister for 60 min at room temperature under constant stirring at a speed of 1000 rpm. After extraction, the twister was removed from the sample, dried with filter paper, inserted into a glass tube and then introduced in a thermodesorber (TDU, Gerstel) for cGC–MS analysis (see Section 2.3). Blank runs were done with each twister before and after each analysis and no memory effects were observed. Each experiment was repeated three times.

2.4. HSSE and SBSE-thermal desorption-cGC–MS analysis

Analyte thermal desorption from twisters was carried out with a TDU unit from Gerstel installed on a Agilent 6890 GC unit coupled to an Agilent 5973N MSD. For the TDU the following parameters were used: desorption programme: from 30 to 250 °C (5 min) at 60 °C/min; flow mode: splitless, transfer line: 250 °C. A Gerstel CIS-4 PTV injector was used to focus cryogenically the analytes thermally desorbed from the stir bar. The PTV was cooled to −50 °C using liquid CO_2; injection: PTV; injection temperature: from −50 °C to 250 °C (5 min) at 12 °C/s. Inlet was operated in the splitless mode for coffee and atrazine standard solution and in the split mode for sage (split ratio 1:10) and for wiskey (split ratio 1:20).

Capillary GC–MS analyses were performed on an Agilent 6890 GC-5973N MS system (Agilent, Little Falls, DE, USA).

2.4.1. Chromatographic conditions

- Coffee analysis
  Column: FSOT Carbowax 20M (d_f 0.25 μm, i.d. 0.25 mm, length: 30 m) (Mega, Legnano (Milano), Italy). Temperature programme: from 70 °C (1 min) to 100 °C at 20 °C/min then to 220 °C (5 min) at 3 °C/min.
- Sage leaves analysis
  Column: FSOT SE 52 (d_f 0.25 μm, i.d. 0.25 mm, length: 30 m) (Mega, Legnano (Milano), Italy). Temperature programme: from 50 °C (1 min) to 220 °C (5 min) at 3 °C/min.
- Wiskey analysis
  Column: FSOT HP-5MS (d_f 0.25 μm, i.d. 0.25 mm, length: 30 m). Temperature programme: from 50 °C (1 min) to 250 °C (1 min) at 5 °C/min.
- 1 ppb atrazine standard solution analysis
  Column: HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm). Temperature programme: from 120 °C (0.1 min) to 280 °C (1 min) at 7 °C/min.

For all experiments the carrier gas was helium, flow-rate: 1.0 mL/min, in constant flow mode. MS was in EI mode at 70 eV. Ion source temperature: 250 °C. The HS and wiskey components were identified by the comparison of their mass spectra with those of authentic samples or with data in the literature.

3. Results and discussion

Sorptive extraction with dual-phase twisters involves three main steps: a sorption of the analyte(s) onto PDMS from liquid or vapour phase, followed by its (their) diffusion through the PDMS layer and by its (their) absorption onto the inner phase. The total recovery of an analyte is therefore conditioned by its affinity for PDMS (i.e. polarity and $K_{o/w}$), its diffusivity through it and its affinity for the adsorbing material. The analyte(s)/inner phase interaction must be reversible to afford its (their) successive thermal desorption. Several HSSE and SBSE experiments involving carbons and PDMS (see Section 2.1) with different characteristics were therefore carried out to meet the above requirements.

3.1. HSSE with dual-phase twisters

The performance of dual-phase twisters for HSSE sampling was evaluated by analyzing the head space composition of two matrices, i.e. coffee and dried sage (*S. officinalis* L.) leaves.

HSSE experiments were carried out under unfavourable phase ratio conditions (50 and 5 mg for coffee and sage, respectively, in 250 mL) in view of further applications to study biological phenomena involving headspace sampling of analytes in traces. Fig. 2 reports the TDU-cGC–MS profiles of roasted Costa Rica coffee after HSSE sampling with a conventional twister, an empty 0.5 mm thick PDMS twister and a dual-phase 0.5 mm thick PDMS twister packed with RR carbon. Fig. 3 reports the TDU-cGC–MS profiles of a sage (*S. officinalis*) after HSSE sampling with a conventional twister, an empty 0.5 mm thick PDMS twister and a dual-phase 0.5 mm thick PDMS twister filled (packed) with BB carbon. From the TDU-cGC–MS profiles, the increased concentration capability of dual-phase twisters is evident as well as the difference between RR carbon and BB carbon. RR carbon is very effective with highly volatile components while BB carbon is better with the less volatile ones most probably because of their different physico-chemical characteristics. For a better evaluation of the concentration capability of dual-

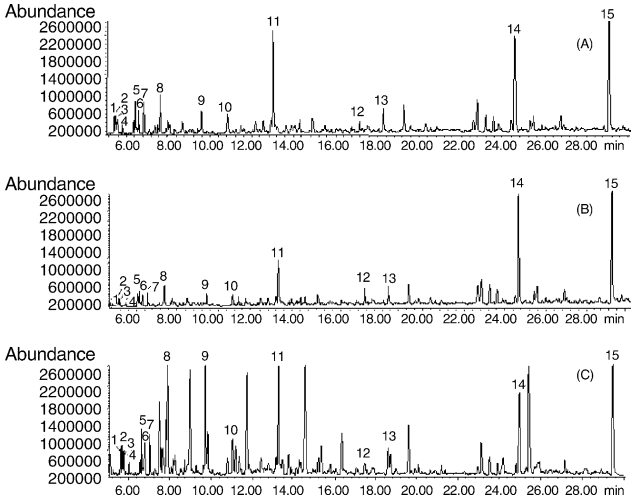

Fig. 2. TDU-cGC–MS profiles of roasted Costa Rica coffee after HSSE sampling with a conventional twister (A), an empty 0.5 mm thick PDMS twister (B) and a dual-phase 0.5 mm thick PDMS twister packed with RR carbon (C). (1) 2,5-Dimethylpyrazine; (2) 2,6-dimethylpyrazine; (3) 2-ethylpyrazine; (4) 2,3-dimethylpyrazine; (5) 2-ethyl-6-methylpyrazine; (6) 2-ethyl-5-methylpyrazine; (7) 2-ethyl-3-methyl pyrazine; (8) 3-ethyl-2,5-dimethylpyrazine; (9) furfuryl acetate; (10) 2-furancarbossialdehyde-5-methyl; (11) furfuryl alcohol; (12) 2-hydroxy-3-methyl-2-cyclopenten-1-one; (13) 1-(2-furfuryl)-pyrrole; (14) *p*-ethylguaiacole and (15) *p*-vinylguaiacole.

phase twisters, and among them of the most effective carbon packings, the concentration factors (CFs) obtained for a set of marker components for both roasted Costa Rica coffee and dried sage leaves were also calculated assuming the conventional twister areas, arbitrarily taken as 100, as a reference. Table 1 reports the list of the selected markers for both roasted

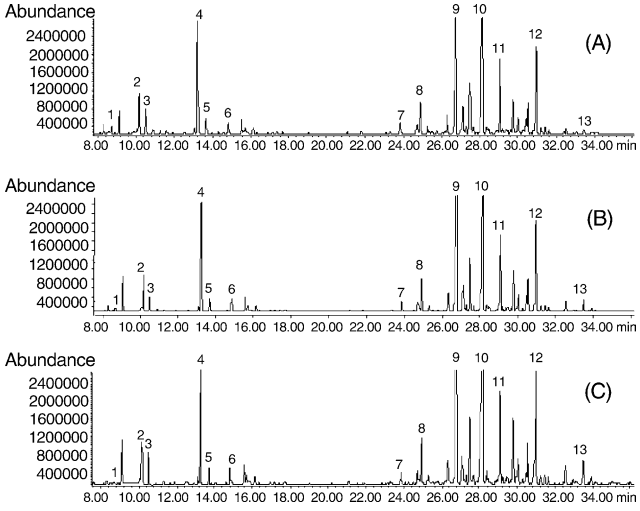

Fig. 3. TDU-cGC–MS profiles of a sage (*Salvia officinalis* L.) after HSSE sampling with a conventional twister (A), an empty 0.5 mm thick PDMS twister (B) and a dual-phase 0.5 mm thick PDMS twister packed with BB carbon (C). (1) β-Myrcene; (2) 1,8-cineole; (3) *cis*-β-ocimene; (4) α-thujone; (5) β-thujone; (6) camphor; (7) α-cubebene; (8) α-copaene; (9) β-caryophyllene; (10) α-humulene; (11) γ-muurolene; (12) δ-cadinene and (13) viridiflorol.

Table 1
List of markers chosen for both roasted Costa Rica coffee and dried sage leaves

N	Roasted Costa Rica coffee	Dried sage leaves
1	2,5-Dimethylpyrazine	β-Myrcene
2	2,6-Dimethylpyrazine	1,8-Cineole
3	2-Ethylpyrazine	*cis*-β-Ocimene
4	2,3-Dimethylpyrazine	α-Thujone
5	2-Ethyl-6-methylpyrazine	β-Thujone
6	2-Ethyl-5-methylpyrazine	Camphor
7	2-Ethyl-3-methyl pyrazine	α-Cubebene
8	3-Ethyl-2,5-dimethylpyrazine	α-Copaene
9	Furfuryl acetate	β-Caryophyllene
10	2-Furancarbossialdehyde-5-methyl	α-Humulene
11	Furfuryl alcohol	γ-Muurolene
12	2-Hydroxy-3-methyl-2-cyclopenten-1-one	δ-Cadinene
13	1-(2-Furfuryl)-pyrrole	Viridiflorol
14	*p*-Ethylguaiacole	
15	*p*-Vinylguaiacole	

Costa Rica coffee and dried sage leaves. The concentration factor is the ratio between the areas of a marker obtained by HSSE with empty and dual-phase twisters and that obtained by the conventional twister with a PDMS volume determined under the same sampling conditions. CF is useful to evaluate the relative recovery effectiveness of different twisters for a given sample, provided that rigorous and reproducible analysis conditions are applied.

Table 2 reports the concentration factors of roasted Costa Rica coffee after HSSE sampling with a conventional twister, an empty 0.5 mm thick PDMS twister and the dual-phase 0.5 mm thick PDMS twisters packed with the different carbons. Table 3 reports the concentration factors of sage dried leaves after HSSE sampling with a conventional twister, an empty 0.5 mm thick PDMS twister and the dual-phase 0.5 mm thick PDMS twisters packed with the different carbons. The best recoveries are in italics. These results clearly demonstrate how the nature of the carbon may influence the concentration capability of dual-phase twisters: RR carbon is the only one that improves the recovery of volatile components for both coffee and sage although to different extents depending on the matrix, while BB carbon improves recovery for the less volatile components in sage. The other carbons investigated gave recoveries below those obtained with conventional PDMS twisters. On the other hand, a thicker PDMS tube (1 mm) produces a better recovery for all analytes not only for RR and BB carbons but also for carbon RB, although less pronounced (Table 4). A possible explanation is related to the contribution of the absolute amount of PDMS to the total recovery: higher amounts of PDMS sorbed higher amounts of analytes and, as a consequence, higher adsorption of analytes on carbon, provided that a sampling time suitable to afford the analyte diffusion through PDMS is adopted. Moreover, thin and thick empty twisters were prepared with PDMS polymers with different physico-chemical characteristics thus explaining the differences in the ratio between empty and conventional twisters recoveries reported in Tables 2 and 4.

Table 2
Concentration factors of roasted Costa Rica coffee markers after HSSE sampling with a conventional twister, an empty 0.5 mm PDMS twister and the dual-phase 0.5 mm PDMS twister packed with the different carbons

N	Markers	CV	EMP	RR	RB	BB	BY
1	2,5-Dimethylpyrazine	100	46	*357*	107	55	22
2	2,6-Dimethylpyrazine	100	46	*434*	109	61	24
3	2-Ethylpyrazine	100	74	*614*	152	90	22
4	2,3-Dimethylpyrazine	100	53	*555*	122	91	30
5	2-Ethyl-6-methylpyrazine	100	65	*340*	71	74	28
6	2-Ethyl-5-methylpyrazine	100	60	*238*	79	60	25
7	2-Ethyl-3-methyl pyrazine	100	72	*300*	58	87	33
8	3-Ethyl-2,5-dimethylpyrazine	100	80	*723*	66	103	44
9	Furfuryl acetate	100	56	*1230*	34	30	15
10	2-Furancarbossialdehyde-5-methyl	100	70	*443*	44	35	12
11	Furfuryl alcohol	100	59	*336*	65	38	13
12	2-Hydroxy-3-methyl-2-cyclopenten-1-one	100	78	*100*	47	57	18
13	1-(2-Furfuryl)-pyrrole	100	80	*137*	33	61	12
14	*p*-Ethylguaiacole	100	85	*86*	24	59	22
15	*p*-Vinylguaiacole	100	104	*64*	16	45	25

CV: conventional twisters; EMP: empty dual-phase twister; RR: Carbopack B; RB: Carbopack C; BB: Carbosieve and BY: Carboxen.

Table 3
Concentration factors of sage leave markers after HSSE sampling with a conventional twister, an empty 0.5 mm PDMS twister and the dual-phase 0.5 mm PDMS twister packed with the different carbons

N	Markers	CV	EMP	RR	RB	BB	BY
1	β-Myrcene	100	61	*284*	35	86	17
2	1,8-Cineole	100	88	*257*	77	106	56
3	*cis*-β-Ocimene	100	67	*130*	11	115	8
4	α-Thujone	100	94	*125*	42	118	31
5	β-Thujone	100	92	*190*	33	120	25
6	Camphor	100	107	*251*	78	146	51
7	α-Cubebene	100	90	51	34	*112*	19
8	α-Copaene	100	107	58	38	*158*	23
9	β-Caryophyllene	100	102	70	47	*133*	27
10	α-Humulene	100	103	69	47	*144*	28
11	γ-Muurolene	100	101	60	39	*138*	23
12	δ-Cadinene	100	104	65	39	*141*	25
13	Viridiflorol	100	309	353	359	*631*	304

CV: conventional twisters; EMP: empty dual-phase twister; RR: Carbopack B; RB: Carbopack C; BB: Carbosieve and BY: Carboxen.

Table 4
Concentration factors of roasted Costa Rica coffee markers after HSSE sampling with a conventional twister, an empty 1.0 mm PDMS twister and the dual-phase 1 mm PDMS twister filled with different carbons

N	Markers	CV	EMP	RR	RB	BB	BY
1	2,5-Dimethylpyrazine	100	136	*205*	177	189	86
2	2,6-Dimethylpyrazine	100	131	*191*	111	156	80
3	2-Ethylpyrazine	100	180	228	358	*413*	87
4	2,3-Dimethylpyrazine	100	204	255	90	*293*	77
5	2-Ethyl-6-methylpyrazine	100	109	*149*	126	142	88
6	2-Ethyl-5-methylpyrazine	100	97	137	152	*163*	106
7	2-Ethyl-3-methyl pyrazine	100	120	*129*	54	54	53
8	3-Ethyl-2,5-dimethylpyrazine	100	111	*156*	123	130	70
9	Furfuryl acetate	100	100	*174*	122	130	67
10	2-Furancarbossialdehyde-5-methyl	100	105	*154*	120	116	74
11	Furfuryl alcohol	100	189	*294*	243	189	71
12	2-Hydroxy-3-methyl-2-cyclopenten-1-one	100	121	*165*	149	116	77
13	1-(2-Furfuryl)-pyrrole	100	157	*169*	107	102	56
14	*p*-Ethylguaiacole	100	102	*112*	100	76	62
15	*p*-Vinylguaiacole	100	*116*	98	90	74	76

CV: conventional twisters; EMP: empty dual-phase twister; RR: Carbopack B; RB: Carbopack C; BB: Carbosieve and BY: Carboxen.

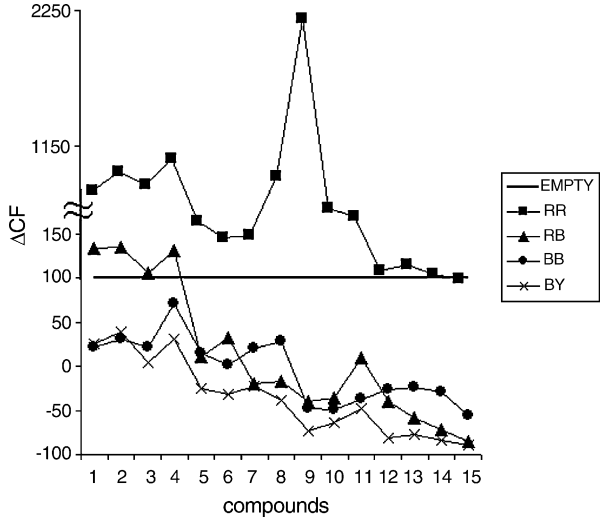

Fig. 4. ΔCFs vs. empty PDMS twister of the markers of roasted Costa Rica coffee when sampled by HSSE with dual-phase twisters packed with the five carbons under investigation.

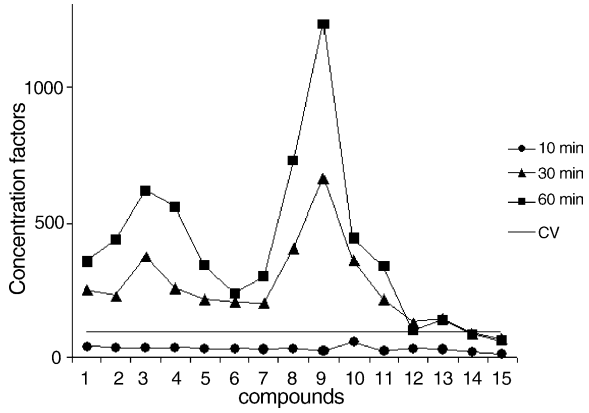

Fig. 5. Evolution of the concentration factors compared to the conventional twister (60 min sampling) of the roasted Costa Rica coffee markers after HSSE with dual-phase twisters packed with RR carbon after 10, 30 and 60 min.

The rigorously standardized operative conditions allowed also us to determine the contribution of each carbon to the total analyte recovery. "*Carbon recovery*" was determined by subtracting the area of each marker obtained with the empty twister from that obtained with each dual-phase twister and calculating the contribution to CF due to each carbon (ΔCF) versus the area of the empty twister taken as 100. Fig. 4 reports ΔCFs of the markers of roasted Costa Rica coffee when sampled by HSSE with dual-phase twisters packed with the four carbons under investigation. In this case too, RR carbon gives the highest contribution to recovery with almost all markers whereas the other carbons influence it negatively, in particular, with the less volatile and/or more polar components, possibly because of their stronger adsorption characteristics preventing analyte thermal release of the analytes.

A series of experiments was also carried out to evaluate the contribution of carbon to the recovery of marker components with respect to time. Fig. 5 reports the evolution of the concentration factors of the roasted Costa Rica coffee markers after HSSE with dual-phase twisters packed with RR carbon after 10, 30 and 60 min. These results show that carbon does not contribute to recovery when sampling time is short but significantly influence it when longer times are adopted (30 or 60 min.). With 10 min samplings, PDMS sorption plays a prominent role probably because the time is not sufficient for the sampled analytes to diffuse through PDMS and to reach the carbon packing. This explanation is confirmed by the comparable recoveries of all markers after 10 min sampling with the dual-phase twister and after 1 hour sampling with the conventional twister.

Repeatability and intermediate precision of dual-phase twisters were also determined. Repeatability was measured by analysing six samples of the roasted Costa Rica coffee samples from the same lot and determining the relative standard deviation (RSD%) of the areas (%) of the selected markers. Table 5 reports the mean area percent calculated on the six experiments and repeatability expressed as RSD% of each marker after HSSE sampling with a PDMS 0.5 mm/RR carbon dual-phase twister. Repeatability is very satisfactory with RSD% ranging from 0.2 for furfuryl alcohol to 13.4 for 2,6-dimethylpyrazine.

Intermediate precision was measured by sampling the headspace of the roasted Costa Rica coffee sample by HSSE with a set of five RR carbon/1 mm PDMS twisters. Experiments for each dual-phase twisters were repeated three times. Table 5 also reports intermediate precision data expressed as RSD% and mean area percent of each marker of the roasted Costa Rica coffee sample after HSSE sampling referred to the five dual-phase twisters. These results show that intermediate precision too is good with RSD% ranging from 3.2 for furfuryl acetate to 16.9 for 2-ethylpyrazine.

3.2. SBSE with dual-phase twisters

Some preliminary SBSE with dual-phase twisters experiments were carried out.

The first application concerns the analysis of a commercially available sample of whiskey tested for qualitative purposes. A whiskey sample 10-fold diluted with water (1 mL + 9 mL water) was submitted to SBSE with both a 1.0 cm × 0.5 mm conventional twister and a RR carbon/0.5 mm PDMS dual-phase twister of the same length. Fig. 6(A) reports the TDU-cGC–MS profiles of the whiskey after SBSE sampling with conventional (a) and RR carbon/0.5 mm PDMS dual-phase twisters (b). Both twisters gave qualitatively similar chromatograms, but some quantitative differences can be observed. For instance, the carbon contribution to the recovery of polar compounds is evident with lauric acid (5) and ethyl laurate (6). While the ester abundance is approximately the same in both chromatograms, the recovery of the more polar acid is significantly better with carbon/PDMS dual-phase twister. The difference in recovery is even more pronounced for the early eluting components

Table 5
Repeatability of PDMS 0.5 mm/RR carbon dual-phase twister determined on the roasted Costa Rica coffee markers after HSSE sampling

N	Markers	t_R	Repeatability		Intermediate precision	
			Area (%)	RSD (%)	Area (%)	RSD (%)
1	2,5-Dimethylpyrazine	5.21	1.2	4.9	1.1	8.0
2	2,6-Dimethylpyrazine	5.29	1.5	13.4	1.3	3.7
3	2-Ethylpyrazine	5.37	0.6	7.8	0.6	16.9
4	2,3-Dimethylpyrazine	5.64	0.4	9.5	0.4	16.3
5	2-Ethyl-6-methylpyrazine	6.22	1.1	4.6	1.0	1.4
6	2-Ethyl-5-methylpyrazine	6.29	0.7	5.1	0.8	10.8
7	2-Ethyl-3-methyl pyrazine	6.44	1.2	8.2	1.2	6.0
8	3-Ethyl-2,5-dimethylpyrazine	7.53	0.6	2.3	0.6	8.9
9	Furfuryl acetate	9.61	0.9	1.5	1.0	3.2
10	2-Furancarbossialdehyde-5-methyl	10.86	2.5	12.4	2.4	8.1
11	Furfuryl alcohol	13.11	22.8	0.2	22.0	10.1
12	2-Hydroxy-3-methyl-2-cyclopenten-1-one	17.31	1.8	1.9	1.7	7.5
13	1-(2-Furfuryl)-pyrrole	18.45	1.8	11.6	1.8	6.7
14	*p*-Ethylguaiacole	24.83	2.1	4.3	2.0	14.6
15	*p*-Vinylguaiacole	29.39	7.4	2.7	7.2	16.1

Area (%) and RSD (%) were measured on $n = 6$ experiments. Areas (%) and intermediate precision determined on the roasted Costa Rica coffee markers after HSSE sampling with five PDMS 1.0 mm/RR carbon dual-phase twisters.

as shown in Fig. 6(B), in which the first part of the chromatograms is zoomed. For instance, with a conventional twister isoamyl alcohol (1) and iso-amylacetate (2) are nearly absent in the cGC–MS profile and phenethyl alcohol (4) is only present as a trace. The recovery of the last compound ($\log P = 1.36$ and calculated theoretical recovery: 5% [1,30]) with carbon/PDMS dual-phase twister is at least 10 times higher.

The second application concerns the evaluation of the concentration capability of dual-phase twisters on ultratraces, again for qualitative purposes. A 10 mL sample spiked at 1 ppb with atrazine was submitted to SBSE with both a conventional and a RR carbon/0.5 mm PDMS dual-phase twister (1.0 cm). After sampling, the recovered atrazine was thermally desorbed (TDU) an on-line analyzed by cGC–MS. Under the conditions adopted, (atrazine log *P*: 2.61; sample volume: 10 mL), the calculated theoretical recovery on PDMS is 49% [1,30]. The relative increase in absolute percent recovery calculated on the atrazine diagnostic ion areas was about 80% higher with a dual-phase twister than with a conventional twister. Fig. 7 reports the ion chromatograms using 200 amu as diagnostic ion for atrazine.

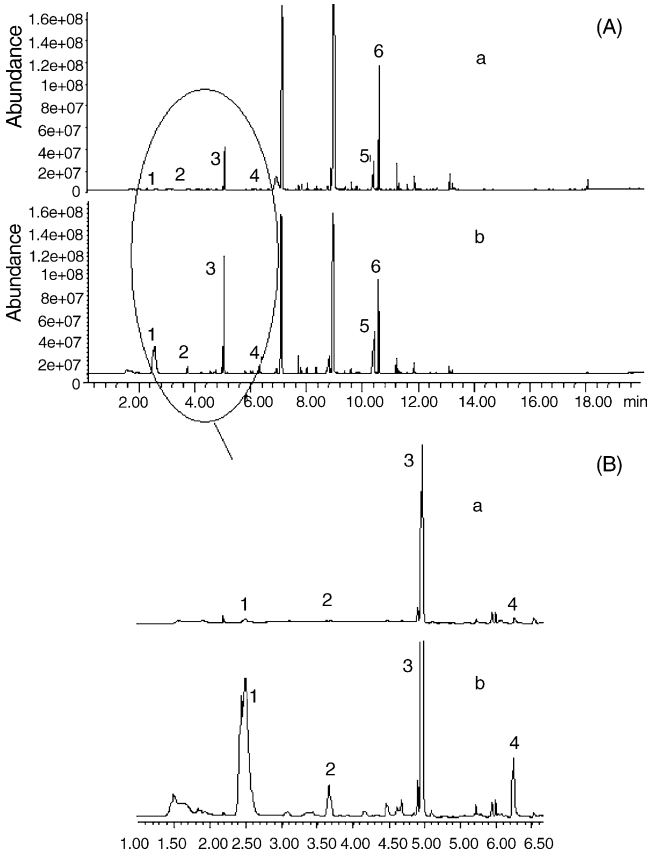

Fig. 6. (A) TDU-cGC–MS profiles of the whiskey after SBSE sampling with conventional (a) and RR carbon/0.5 mm PDMS dual-phase twisters (b). (1) *i*-Amyl alcohol; (2) *i*-amyl acetate; (3) ethyl hexanoate; (4) phenethyl alcohol; (5) lauric acid; (6) ethyl laurate and (B) zoom of the first parts of the chromatograms.

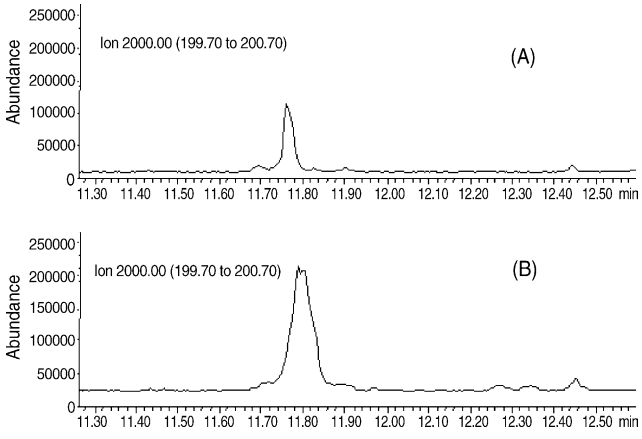

Fig. 7. TDU-cGC–MS ion chromatograms using 200 amu as diagnostic ion for atrazine after SBSE sampling with conventional (a) and RR carbon/0.5 mm PDMS dual-phase twisters (b).

4. Conclusions

Dual-phase twisters packed with different carbons as an additional concentrating phase have here been shown to improve recovery of volatile and/or polar components when compared to conventional PDMS stir bars. Recovery depends on the physico-chemical characteristics of the adsorbing material (carbon) and of the sorption and diffusion capability of PDMS. Several PDMS and carbons are now being screened to select a suitable combination to achieve the highest recovery [31]. The successful combination of two concentrating phases operating with different phenomena (in this case sorption with PDMS and adsorption with carbon) opens new perspectives to selective extraction of classes or groups of compounds. This approach will make it possible to selectively recover an analyte(s) present in traces using a twister packed with an inner phase specific to that analyte(s). Some very preliminary experiments carried out in one of the author's laboratory using dual-phase twisters packed with chromosorb coated with selective reagents have been successful in the selective sampling of aldehydes, ketones, alcohols and thiols [31].

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