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Polymeric ionic liquid coatings *versus* commercial solid-phase microextraction coatings for the determination of volatile compounds in cheeses

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ABSTRACT

The extraction performance of four polymeric ionic liquid (PIL)-based solid-phase microextraction (SPME) coatings has been studied and compared to that of commercial SPME coatings for the extraction of 16 volatile compounds in cheeses. The analytes include 2 free fatty acids, 2 aldehydes, 2 ketones and 10 phenols and were determined by headspace (HS)-SPME coupled to gas chromatography (GC) with flame-ionization detection (FID). The PIL-based coatings produced by UV co-polymerization were more efficient than PIL-based coatings produced by thermal AIBN polymerization. Partition coefficients of analytes between the sample and the coating (K_{fs}) were estimated for all PIL-based coatings and the commercial SPME fiber showing the best performance among the commercial fibers tested: carboxen–polydimethylsyloxane (CAR–PDMS). For the PIL-based fibers, the highest K_{fs} value (1.96 ± 0.03) was obtained for eugenol. The normalized calibration slope, which takes into account the SPME coating thickness, was also used as a simpler approximate tool to compare the nature of the coating within the determinations, with results entirely comparable to those obtained with estimated K_{fs} values. The PIL-based materials obtained by UV co-polymerization containing the 1-vinyl-3-hexylimidazolium chloride IL monomer and 1,12-di(3-vinylimiazolium)dodecane dibromide IL crosslinker exhibited the best performance in the extraction of the select analytes from cheeses. Despite a coating thickness of only 7 μm, this copolymeric sorbent coating was capable of quantitating analytes in HS-SPME in a 30 to 2000 μg L^{-1} concentration range, with correlation coefficient (R) values higher than 0.9938, inter-day precision values (as relative standard deviation in %) varying from 6.1 to 20%, and detection limits down to 1.6 μg L^{-1}.

1. Introduction

The determination of volatile compounds in cheeses [1,2] constitutes an interesting tool for obtaining profiles related to aroma composition, which can be linked with further studies regarding cheese quality, cheese origin or even cheese sensorial attributes [3].

Headspace solid-phase microextraction (HS-SPME) [4] is currently the analytical technique of choice in the analysis of food aroma [5,6]. The technique possesses a number of advantages such as eliminating the consumption of organic solvent during the extraction step; combining extraction and preconcentration into one step, ease of automation, and high enrichment factors, among others. The study of complex mixtures of volatile compounds (around a thousand compounds) in foods was successfully carried out when HS-SPME was used in combination with two-dimensional gas chromatography (GC × GC) [7].

The primary commercial SPME coatings employed in the monitoring of volatile compounds in cheeses include carboxen–polydimethylsyloxane (CAR–PDMS) [6,8–10] and divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS) [11,12]. In general, the DVB–CAR–PDMS coating exhibits better extraction performance for medium and high molecular-weight compounds, while the CAR–PDMS coating has shown better results for low molecular-weight compounds [5].

It must be highlighted that a limitation of the SPME technique arises from the relatively small number of coatings commercially available (roughly six). In this sense, there is significant interest to

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develop specific SPME coatings when highly complex extractions are required such as in the case of food aroma, particularly devoted to the extraction of polar analytes (which are in general poorly extracted by commercial coatings). Indeed, the search for novel materials that are good candidates for SPME has recently been a hot topic in the literature [13], and they include ionic liquids (ILs) [14], nanotubes (NTs) [15], and conductive polymers (CPs) [16], among others.

Polymeric ionic liquids (PILs) can be cited as an important group of materials with good abilities as SPME coatings [17]. As defined by Mecerreyes [18]: PILs are polymers synthesized from IL monomers as opposed to polyelectrolytes which are synthesized from solid salt monomers. PILs are quite attractive polymers because they are able to retain several IL properties such as ionic conductivity, thermal stability, and tuneable solvent properties. First described PIL was used as a stationary phase in gas-chromatography [19].

Up to now, the majority of PIL-based SPME coatings have been prepared by coating a linear polymer of the PIL sorbent on the bare silica support. They have been used in both HS-SPME applications [20–25] or in direct immersion (DI-) measurements [26–28]. Very recently, Ho et al. utilized "on-fiber" ultraviolet (UV)-initiated polymerization consisting entirely of monocationic IL monomers and dicationic IL crosslinkers to form crosslinked copolymeric PIL-based SPME coatings [29]. These crosslinked sorbent coatings are chemically bonded to the silica support and have been used in both HS- and DI-SPME for the determination of polar analytes, including alcohols, aldehydes, and esters in waters [29]. Using a different synthetic approach, Wanigasekara et al. have also described the use of silica-bonded ionic liquid derivatives in SPME [30]. Altogether with the development of analytical applications of PILs in SPME, efforts have also been shifted to give insight into the sorption mechanism that takes place when PIL coatings are employed in SPME [31,32].

Due to the unique and tuneable solvent properties of PIL-based coatings, there is enormous interest in exploiting these materials in the determination of volatiles in food samples by HS-SPME. Monocationic linear PIL-based coatings prepared by AIBN polymerization have been used in the determination of volatiles in wines [20] and coffee beans [23]; however, the comparison in these studies was exclusively limited to the commercial polyacrylate (PA) and polydimethylsyloxane (PDMS) coatings. Two recent reports described PIL-based coatings for the determination of volatiles in beers, and compared the results with other commercial SPME coatings [25,30].

The main aim of this work is to deeply compare the extraction performance of four PILs coatings, two of them being prepared by thermal AIBN polymerization and the other two being crosslinked co-polymeric coatings formed by UV polymerization, with that of a variety of commercial SPME coatings including CAR–PDMS. The comparison is carried out for a group of volatile compounds in cheeses using HS-SPME–GC. Selected analytes include volatile free fatty acids, aldehydes, ketones, and phenols. Partition coefficients of these analytes to the SPME coatings have also been obtained to quantitate the selectivity of the examined coatings.

2. Experimental

2.1. Reagents and materials

The studied volatile compounds were free fatty acids (FFAs), carbonyl compounds (aldehydes and ketones) and phenols. Caproic acid, eugenol ($>99.0\%$), guaiacol ($\geq 98.0\%$), 2,6-dimethoxyphenol or syringol ($\geq 97\%$) and 3-methoxyphenol ($\geq 97.0\%$) were supplied by Fluka (Buchs, Switzerland). 2-Heptanone (99.0%), 2-nonanone (99.5%), octanal (99.5%), 2-ethylphenol (99.5%) and 3-ethylphenol (97.5%) were purchased from Dr. Ehrenstorfer GmbH (Ausburg, Germany). *p*-Tolualdehyde (97%), *o*-cresol ($\geq 99\%$), *m*-cresol (99%), *p*-cresol (99%) and heptanoic acid were supplied by Sigma-Aldrich (Steinheim, Germany). Phenol was supplied by Merck (Darmstadt, Germany). Sodium chloride ($>99.5\%$) was supplied by Sigma-Aldrich. Ultrapure water was obtained from a Milli-*Q* water purification system (Millipore, Watford, UK).

All analytes were dissolved in acetonitrile (Merck) to obtain individual standards, with concentrations of 1900 mg L^{-1}, being of 973 mg L^{-1} for octanal.

These individual solutions were used to prepare a working solution containing 2.5 mg L^{-1} of 2-heptanone and 2-nonanone; 5.0 mg L^{-1} of heptanoic acid, *p*-tolualdehyde, phenol, *o*-cresol and eugenol; 7.0 mg L^{-1} of caproic acid, octanal, *p*-cresol, 2-ethylphenol, 3-ethylphenol and guaiacol; 10.0 mg L^{-1} of *m*-cresol and 3-methoxyphenol; and 12.0 mg L^{-1} of 2,6-dimethoxyphenol, in ultrapure water. The acetonitrile content of the working aqueous solution was 5.4% (v/v). All solutions were stored at 4 °C before use. This working solution was used in the optimization study.

Individual standards were used to prepare two intermediate solutions containing all analytes, with concentrations of 50 and 380 mg L^{-1} in acetonitrile. HS-SPME calibration working solutions (between 30 and 3000 μg L^{-1}) were prepared by dissolving adequate aliquots of these intermediate solutions in a saturated sodium chloride solution, adjusting the acetonitrile content to 1.0% (v/v).

The estimation of the partition coefficients also required the preparation of individual standard solutions in cyclohexane (Sigma-Aldrich), with the following concentrations: 3240 mg L^{-1} for caproic acid, 2888 mg L^{-1} for heptanoic acid, 2000 mg L^{-1} for 2-heptanone, 2-nonanone, *p*-tolualdehyde, phenol, *o*-cresol, *m*-cresol, *p*-cresol, eugenol, guaiacol, 2,6-dimethoxyphenol and 3-methoxyphenol, 1500 mg L^{-1} for 2-ethylphenol and 3-ethylphenol, and 973 mg L^{-1} for octanal. Aliquots of these solutions were used to prepare calibration working solutions, also in cyclohexane, with concentrations of analytes ranging between 1 and 30 mg L^{-1}.

Cheese samples were purchased in local supermarkets. They were smoked and semi-ripened cheeses made with a mixture of goat and ewe pasteurized milks. For SPME experiments, the outer surface was discarded and a piece of 2 cm in depth × 5 cm^2 of surface was selected. The piece was adequately blended and stored in the freezer until analysis.

Amber glass vials (7 mL) with PTFE/Butyl septa screwcaps supplied by CTC Analytics (Zwingen, Switzerland) and a metallic block thermostat (Termobloc, Barcelona, Spain) including a support for SPME fibers were used in all SPME experiments. The 10 mL amber glass vials with PTFE/Butyl septa screwcaps and a Combi-Pal autosampler (CTC Analytics) were used in liquid injection experiments.

The reagents used for the synthesis of the PILs were: 1-vinylimidazole, hexadecyl chloride, 2,2′-azo-bis(isobutyronitrile) (AIBN), imidazole, acrylonitrile ($>99\%$), ammonium hydrogen difluoride, 4-vinylbenzyl chloride (97%), 1-chlorohexane, 2-hydroxy-2-methylpropiophenone (DAROCUR 1173), 1-bromohexadecane, 1,8-dibromooctane, 1,12-dibromododecane, and vinyltrimethoxysilane (VTMS), which were supplied by Sigma-Aldrich. Lithium bis[(trifluoromethyl)sulfonyl]imide (Li-NTf_2) was acquired to SynQuest Labs (Alachua, FL, USA). Isopropanol, *n*-hexane, acetone, dichloromethane, methanol, chloroform, ethyl acetate and sodium hydroxide were purchased at Fisher Scientific (Fair Lawn, NJ, USA).

Four PIL-based SPME fibers were used. The characteristics of these SPME coatings are shown in Table 1. Homemade SPME fiber devices was constituted by a fused silica capillary tubing of 0.1 mm internal diameter (I.D.) for Fiber A and Fiber B, supplied by Supelco (Bellefonte, PA, USA), and of 0.05 mm I.D. for Fiber C and Fiber D,

Table 1
Characteristics of the PIL-based SPME sorbent coatings used in this study.

Coating abbreviation	Polymerization type	IL monomer	Cross-linker (dicationic IL)	Radical initiator	Film thickness (μm)	Coating volume (μL)
Fiber A	Thermal	$ViC_{16}Im\text{-}NTf_2$[a]	–	AIBN[b]	~20	0.161
Fiber B	Thermal	$ViBzC_{16}Im\text{-}NTf_2$[c]	–	AIBN[b]	~12	0.094
Fiber C	UV	$ViC_6Im\text{-}Cl$[d]	$(ViIm)_2C_{12}\text{-}2Br$[e]	DAROCUR 1173[f]	~7	0.035
Fiber D	UV	$ViC_6Im\text{-}Cl$[d]	$(ViIm)_2C_8\text{-}2Br$[g]	DAROCUR 1173[f]	~7	0.035

[a] 1-Vinyl-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide.
[b] 2,2′-Azobis(2-methylpropionitrile).
[c] 1-(4-Vinylbenzyl)-3-hexadecylimidazolium bis[(trifluoromethyl)sulfonyl]imide.
[d] 1-Vinyl-3-hexylimidazolium chloride.
[e] 1,12-Di(3-vinylimidazolium)dodecane dibromide.
[f] 2-Hydroxy-2-methylpropiophenone.
[g] 1,8-Di(3-vinylimidazolium)octane dibromide.

supplied by Polymicro Technologies (Phoenix, AZ, USA). The capillaries were inserted in a 5 μL Hamilton syringe (Reno, NV, USA) and attached with epoxy glue to the plunger.

Commercial SPME fibers of polyacrylate (PA, 85 μm of film thickness), polydimethylsiloxane (PDMS, 30 μm of film thickness), divinylbenzene/carboxen–polydimethylsiloxane (DVB/CAR–PDMS, 50/30 μm of film thickness), and carboxen–polydimethylsiloxane (CAR–PDMS, 75 μm of film thickness), were obtained from Supelco.

2.2. Instrumentation

The preparation of crosslinked co-polymeric PIL-based sorbent coatings required a RPR-100 UV reactor with spinning carousel supplied by Southern New England Ultraviolet Company (Bradford, Connecticut, USA). The UV reactor utilized 16 lamps that produced 254 nm radiation.

The separation and quantification of volatile analytes were performed using a Varian 450 model CP-3800 gas chromatograph (GC) equipped with a flame ionization detector (FID), and a FFAP CB column (25 m × 0.32 mm I.D., 0.30 μm film thickness) supplied by Agilent Technologies (Amstelveen, Holland). The carrier gas was nitrogen, with a flow-rate of 2 mL min^{-1}. The temperature of the injector depended on the SPME fiber used (to avoid decomposition): 280 °C for PA, PDMS and CAR–PDMS, 270 °C for DVB/CAR-PDMS, 250 °C for Fiber A and Fiber B, and 165 °C for Fiber C and Fiber D. The desorption time for the fibers in the GC was 6 min in all cases, to avoid carry over.

GC injection was performed under splitless mode in both SPME and liquid injection analysis. In both cases, an inlet sleeve, glass, single gooseneck liner (MD-24-12-1), from Varian, was used. The following GC oven temperature program was employed: 40 °C, 2 min isothermal, then 25 °C min^{-1} up to 130 °C, and then 20 °C min^{-1} up to 240 °C. The FID detector was kept at 280 °C, using an air flow of 300 mL min^{-1}, a make-up flow of nitrogen of 30 mL min^{-1}, and a hydrogen flow of 30 mL min^{-1}. MS workstation 6.9.3 Software (Varian) was used for data acquisition.

2.3. SPME procedure

PIL-based SPME coatings used in this study were synthesized and characterized as described in previous publications [20,22,27]. PIL-based fibers can be separated in two groups according to the polymerization method used to generate the coatings. The sorbents coatings used for Fiber A and Fiber B were synthesized by thermal AIBN polymerization to form linear polymers using different IL monomers ($ViC_{16}Im\text{-}Cl$ for Fiber A and $ViBzC_{16}Im\text{-}Cl$ for Fiber B). To increase the thermal stability of the PIL coatings, the halide anions were exchanged by the bis[(trifluoromethyl) sulfonyl]imide (NTf_2^-) anion using lithium bis[(trifluoromethyl) sulfonyl]imide as the anion exchange reagent. The PIL-based sorbent coatings were then coated on the fused silica support. Fiber C and Fiber D were produced using "on fiber" photoinitiated copolymerization [29]. The $ViC_6Im\text{-}Cl$ IL monomer was combined with different IL cross-linkers ($(ViIm)_2C_{12}\text{-}2Br$ for Fiber C and $(ViIm)_2C_8\text{-}2Br$ for Fiber D) to generate the crosslinked PIL-based coating. In both cases, DAROCUR 1173 UV photoinitiator was used to generate the coatings. This second group of SPME fibers can be described as crosslinked co-polymeric PIL-based sorbent coating chemically bonded to the silica support.

All SPME extractions (with PIL-based or commercial coatings) were conducted in headspace mode. When working with standards, experiments utilized 1 mL of working solution or calibration working solutions. When working with real samples, 0.5 g of cheese were placed in the vial with 1 mL of saturated NaCl solution. Optimum extraction conditions were conducted by exposure of the SPME coating fiber in the HS of the vial at 45 °C during 40 min. After each working day, an extra-cleaning step was carried out by exposing SPME fibers to the GC injector for 10 min at the corresponding desorption temperature.

The glassware used in this study were first washed with detergent and tap water and then, with a mix of Derquim-Oxy supplied by Panreac (Barcelona, Spain) and sulfuric acid purchased from Sigma-Aldrich. The non-graduated glassware and the vials were dried in an oven at 550 °C during 2.5 h.

2.4. Estimation of partition coefficients in HS-SPME

Two partition equilibria take place during the extraction in HS-SPME: (1) between the sample and the headspace (represented by the partition coefficient K_{gs}); and (2) between the coating and the headspace (represented by the partition coefficient K_{fg}). The amount of analyte on the fiber after the extraction (n_f) can be obtained by Eq. (1) [33] if considering equilibrium conditions and an ideal gas behavior for the group of analytes studied

$$n_f = \frac{K_{fs} c_0 V_f V_s}{K_{fs} V_f + K_{gs} V_g + V_s} \quad (1)$$

where K_{fs} is the partition coefficient of the analyte between the coating and the sample ($K_{fs}=K_{gs} \times K_{fg}$); c_0 is the initial concentration of the analyte in the sample vial, extracted via HS-SPME (in mg L^{-1}); and V_f, V_s and V_g are the volumes of the coating, the sample and the headspace, respectively.

In general, K_{gs} is relatively small for most of the volatile analytes studied. For example (assuming equilibrium conditions that we are not achieving) K_{gs} values according to the Henry's Law [33] are estimated as 0.003 for phenol, 0.09 for octanal and 0.65

for 2-pentanone, as representative examples. Besides, if it is considered that the sample volume is much higher than the volume of the fiber ($V_f \ll V_s$), and that reported K_{fs} values for volatiles are normally below 1000 [33], Eq. (1) can be expressed as

$$n_f = K_{fs} c_0 V_f \quad (2)$$

Thus, Eq. (2) can be used as a simple way to estimate K_{fs} for the group of analytes studied. It must be highlighted that it is proposed here a simple estimation of partition coefficient values, and not an absolute determination (out of the purpose of the work).

3. Results and discussion

3.1. Optimization of the HS-SPME-GC-FID method

The selected group of sixteen volatile compounds monitored in cheese samples by HS-SPME–GC–FID using commercial and PIL-based sorbent coatings, included: 2 free fatty acids, 2 aldehydes, 2 ketones and 10 phenols. GC separation was successfully accomplished using the experimental conditions described in Section 2.2, with phenol and *o*-cresol being the only analytes that could not be resolved; therefore, their quantification was accomplished as a mixture (phenol + *o*-cresol). Under optimized conditions, the reproducibility of the retention times for the studied analytes ranged between 0.3 and 1.5% (Table S1 of the Supplementary materials).

The main factors influencing the extraction efficiency in HS-SPME, for a given coating, are the extraction temperature and the extraction time if considering that salting-out is an obvious adequate factor for HS analysis, and that the ratio sample volume/headspace volume is commonly fixed for a certain application. The extraction profiles were studied using the commercial CAR–PDMS fiber and the PIL-based coating (Fiber C). They were selected because it was possible to work at the highest injection temperature (280 °C) with the CAR–PDMS fiber, whereas the lowest injection temperature is required for Fiber C (165 °C). Lower desorption temperatures can be accompanied by lower sensitivity for certain peaks and even inadequate peak shape. By selecting these two fibers, working at the minimum and maximum injector temperatures, conclusions can be extrapolated for the remaining coatings.

HS-SPME extraction profiles were obtained utilizing 1 mL of aqueous working standard solution in the vial (with saturated NaCl solution to favor the salting-out effect), and analytes content varying from 2.5 to 12.0 mg L^{-1} as described in Section 2.1. Relatively large contents were used in this optimization section because it was simply intended a screening to find best working conditions. Extraction times were studied between 15 and 60 min at a constant extraction temperature of 45 °C, and extraction temperatures were studied between 40 and 60 °C at a constant extraction time of 45 min, using the chromatographic peak area as an estimate of the extraction efficiency. These profiles have been included as Supplementary materials in Figs. S1 and S2, for representative analytes of each family of volatile compounds. For the CAR–PDMS coating, increases in the temperature were clearly accompanied by higher extraction efficiencies, whereas for the PIL Fiber C there was a decrease in the extraction efficiencies at high temperatures, especially at 60 °C. Therefore, an intermediate extraction temperature of 45 °C was selected to compare extraction efficiencies for a variety of analytes among the coatings of different nature. With regards to the extraction time, the ideal situation in SPME is to work under equilibration conditions to obtain the maximum extraction efficiencies. Nevertheless, with the purpose of reducing analysis times in SPME, lower extraction times than those required to achieve equilibration can be selected if they provide the necessary analytical sensitivity. Thus, the majority of analytes did not reach equilibration at the highest extraction time considered (60 min) for CAR–PDMS. On the contrary, the majority of the analytes achieved equilibration in ~20 min with PIL Fiber C which can be attributed not only to the different coating nature but mainly to its lower film thickness. Therefore, an intermediate extraction time of 40 min was selected to compare extraction efficiencies for a variety of analytes among coatings of different nature.

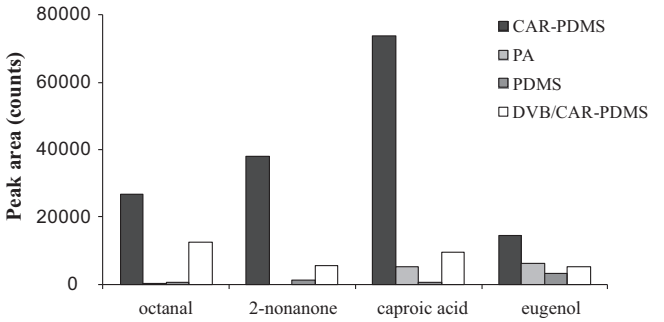

Fig. 1. Comparison of the extraction efficiency, expressed as chromatographic peak areas, for different commercial SPME fibers when determining volatile analytes in cheese using the optimized HS-SPME–GC–FID method. The plot includes representative analytes for each group of volatile compounds.

3.2. Screening of commercial SPME coatings for the determination of volatiles in cheese

The extraction performance of commercial SPME coatings for the determination of the selected group of volatiles was carried out with cheese samples using the above optimized HS-SPME–GC–FID method. The extraction was carried with cheese samples to clearly select the best commercial fiber. Fig. 1 shows the obtained results for the representative analytes for each group of volatile compounds. It can be observed that the highest extraction efficiencies were obtained with the CAR–PDMS fiber. Therefore, the commercial CAR–PDMS fiber was selected to carry out all comparative studies with the PIL-based SPME coatings.

3.3. Estimation of partition coefficients (K_{fs})

The determination of partition coefficients (K_{fs}) for the group of volatile compounds studied is the best tool for comparing the effect that the different coatings have in the overall extraction efficiency of the volatile analytes. The partition coefficient (K_{fs}) refers to the extent of partitioning that analytes undergo between the initial sample (liquid or solid) and the SPME sorbent coating. They have been calculated according to Eq. (2) (Section 2.4), assuming equilibrium conditions among other approximations. Therefore, the partition coefficients obtained here are only approximate values (valid for comparison purposes).

The coating volume (V_f) can be calculated for the PIL-based coatings using the total radius of the fiber coating (the radius of the silica capillary minus film thickness) and the coating length (1 cm). Calculated V_f values for PIL-based coatings are shown in Table 1. For the CAR–PDMS fiber, the V_f value of 1.577 μL was supplied by Supelco.

The n_f values, corresponding to the c_0 values selected, were estimated using the liquid injection calibrations included in Tables S2–S4 of the Supplementary materials. These liquid injection calibration curves were obtained with working solutions in cyclohexane injected in the GC–FID (2 μL), and employing the same injection temperatures which were used in SPME (280, 250 and

165 °C, depending on the fiber coating) to mimic as much as possible desportion conditions in SPME. Cyclohexane was selected as solvent to minimize as much as possible band broadening in direct injection GC when using splitless mode. These calibrations are utilized to calculate the n_f values, using as peak areas those obtained by HS-SPME–GC–FID when extracting an initial concentration of c_0 mg L^{-1}.

It can be considered that the log K_{fs} obtained in this study are only approximate values because we are not working under equilibration conditions. In addition, the n_f values have been estimated by an external calibration method. Besides, the estimated volume of the PIL-based coatings is only an approximation. However, the results are completely valid to evaluate new crosslinked, co-polymeric PILs-based materials as SPME coatings because all partition coefficients (K_{fs}) are calculated using the same conditions.

It must be also considered that the extraction mechanism for these PIL-based SPME fibers should be carefully considered. The above expressions are valid if an absorption mechanism takes place. If these coatings are extracting analytes via an adsorption mechanism, there is a limited number of free sites in the coatings that can be occupied by the analyte molecules [34]. This would require a different set of equations to obtain the partition coefficients related to the Langmuir isotherm, and may not reveal a linear correlation between n_f and c_f. In any case, as long as the initial concentration of analyte in the sample is low, the concentration of analyte in the fiber at equilibrium is lower than the maximum concentration in the fiber (when all the sites are occupied), and so Eq. (2) is valid to predict K_{fs}.

The obtained partition coefficients using Eq. (1) for PIL-based coatings and the commercial CAR–PDMS fiber are shown in Table 2. The K_{fs} values using HS-SPME are determined for the first time for this group of analytes and SPME coatings. The log K_{fs} values of 2-heptanone, octanal, 2-nonanone and *p*-tolualdehyde could not be determined for the crosslinked PIL-based sorbents coatings chemically bonded to the silica (Fiber C and Fiber D), mainly due to integration interferences in the liquid injection calibration curves (Table S4), associated to a high band broadening of cyclohexane when injecting in splitless mode at low injector temperatures (165 °C). In these two fibers, the halide anions dictate a lower injection temperature to prevent decomposition of the PIL.

The comparison of log K_{fs} values was therefore carried out for the remaining analytes to which the log K_{fs} values could be estimated using all SPME fibers (that is, excluding 2-heptanone, octanal, 2-nonanone and *p*-tolualdehyde). Thus, they vary between 0.84 ± 0.05 for 2,6-dimethoxyphenol and 1.92 ± 0.01 for *m*-cresol when using the commercial CAR–PDMS fiber; between 0.42 ± 0.06 for 3-methoxyphenol and 1.66 ± 0.02 for heptanoic acid when employing the PIL-based Fiber A; between 0.86 ± 0.07 for phenol+*o*-cresol and 1.88 ± 0.02 for heptanoic acid when using the PIL-based Fiber B; between 1.25 ± 0.08 for 2,6-dimethoxyphenol and 1.96 ± 0.03 for eugenol when using the PIL-based Fiber C; and between 0.95 ± 0.19 for guaiacol and 1.67 ± 0.06 for heptanoic acid when using the PIL-based Fiber D. For PIL-based fibers, best results were obtained for Fiber C, which exhibited log K_{fs} values higher or similar to the commercial CAR–PDMS coating for the overall group of analytes, except for guaiacol.

If only the crosslinked co-polymeric PIL-based sorbent (Fiber C and Fiber D) are compared with the commercial CAR–PDMS fiber, higher values of log K_{fs} are obtained for caproic acid, heptanoic acid, 2-ethylphenol, eugenol, 3-ethylphenol, 2,6-dimethoxyphenol and 3-methoxyphenol with Fiber C; and for heptanoic acid, 3-ethylphenol, 2,6-dimethoxyphenol and 3-methoxyphenol with Fiber D. Similar log K_{fs} are obtained for the remaining analytes with the three fibers. These results show that the extraction efficiency of the crosslinked PIL-based sorbent coatings is similar to or higher than that obtained with the commercial CAR–PDMS.

If the PIL-based sorbent coatings produced by AIBN polymerization (Fiber A and Fiber B) are compared with CAR–PDMS, higher values are obtained with both PIL-based fibers for heptanoic acid. In addition, Fiber B presented better extraction efficiency than the commercial CAR-PDMS fiber for eugenol, 3-ethylphenol and 2,6-dimethoxyphenol, and similar efficiency to CAR-PDMS for 3-methoxyphenol. This is likely due to the incorporation of the benzyl moiety within this PIL-based coating, which enhanced π–π interaction between analytes and the fiber.

If the log K_{fs} values are correlated with their corresponding log octanol–water partition coefficients (log K_{ow}), determination coefficients (r^2) values of 0.74 for Fiber C, of 0.50 for Fiber A, of 0.46 for Fiber B, of 0.22 for Fiber D, and of 0.17 for CAR–PDMS, are obtained. These results could indicate that for PIL-based Fiber C and Fiber A (r^2 values higher than 0.5), the extraction is mainly

Table 2
Estimated partition coefficients (as log K_{fs}) for the group of volatile compounds and SPME fibers studied.

Analyte	Log $K_{fs} \pm$ error[a]					Log K_{ow}[b]
	CAR–PDMS (75 μm)	Fiber A (~20 μm)	Fiber B (~12 μm)	Fiber C (~7 μm)	Fiber D (~7 μm)	
2-Heptanone	3.05 ± 0.01	1.83 ± 0.01	1.43 ± 0.02	nd[c]	nd[c]	2.00
Octanal	3.12 ± 0.01	2.29 ± 0.01	1.87 ± 0.02	nd[c]	nd[c]	2.95
2-Nonanone	2.64 ± 0.02	2.44 ± 0.01	1.93 ± 0.03	nd[c]	nd[c]	3.02
p-Tolualdehyde	2.86 ± 0.01	0.56 ± 0.18	0.69 ± 0.22	nd[c]	nd[c]	1.90
Caproic acid	1.60 ± 0.03	1.17 ± 0.02	1.39 ± 0.02	1.63 ± 0.05	1.54 ± 0.07	1.72
Guaiacol	1.87 ± 0.01	0.66 ± 0.05	0.90 ± 0.05	1.32 ± 0.09	0.95 ± 0.19	1.34
Heptanoic acid	1.27 ± 0.07	1.66 ± 0.02	1.88 ± 0.02	1.93 ± 0.04	1.67 ± 0.06	2.23
Phenol+*o*-cresol	1.78 ± 0.01	0.51 ± 0.09	0.86 ± 0.07	1.61 ± 0.06	1.13 ± 0.17	1.54
2-Ethylphenol	1.55 ± 0.01	1.02 ± 0.01	1.31 ± 0.01	1.75 ± 0.01	1.22 ± 0.03	2.47
p-Cresol	1.61 ± 0.01	0.57 ± 0.06	0.91 ± 0.05	1.60 ± 0.04	1.15 ± 0.12	2.07
m-Cresol	1.92 ± 0.01	0.77 ± 0.03	1.12 ± 0.02	1.82 ± 0.02	1.35 ± 0.06	2.04
Eugenol	1.53 ± 0.01	1.55 ± 0.01	1.86 ± 0.01	1.96 ± 0.03	1.49 ± 0.08	2.40
3-Ethylphenol	1.25 ± 0.01	0.98 ± 0.01	1.31 ± 0.01	1.82 ± 0.01	1.39 ± 0.02	2.55
2,6-Dimethoxyphenol	0.84 ± 0.05	0.79 ± 0.03	1.14 ± 0.02	1.25 ± 0.08	1.21 ± 0.08	1.22
3-Methoxyphenol	0.99 ± 0.02	0.42 ± 0.06	0.95 ± 0.03	1.35 ± 0.07	1.32 ± 0.08	1.83

[a] Error in the determination of log K_{fs} (calculated from the error in the prediction of n_f, with α=0.05 and m+n-3 degrees of freedom, being m the number of replicates and n the calibration levels; and considering the mathematical propagation of errors when using logarithms. The detailed description of this calculation is included in the Supplementary Materials).

[b] Octanol-water partition coefficients, expressed as log K_{ow} (values extracted from SciFinder® database 2013).

[c] Not determined, with reasons detailed in the text.

taking place by hydrophobic interactions between the studied analytes and the coatings. The extraction mechanism involved when using Fiber B, CAR–PDMS, or Fiber D, must rely on other interactions. Besides, if FFAs and carbonilic compounds are the only ones considered for the comparison with octanol–water partition coefficients, higher r^2 values are obtained with Fiber A (being of 0.71). On the other hand, if only phenolic compounds are studied, Fiber C presented higher correlation with r^2 values of 0.79.

3.4. Analytical performance of the HS-SPME–GC–FID method

HS-SPME–GC–FID calibration curves for each analyte were obtained under optimized conditions using the best fibers according to the log K_{fs} values obtained, that is, for PIL-based Fiber C and Fiber D. For comparative purposes, calibration curves were also obtained with the commercial fiber CAR–PDMS. Tables 3–5 include analytical figures of merit of such calibrations. Concentration ranges used in these calibrations are valid for real sample monitoring (Fig. 3). In all cases, calibration standards were prepared by minimizing the acetonitrile content down to 1.0% (v/v).

It must be considered that the extraction efficiency in SPME is highly affected by the coating thickness [35], whereas partition coefficients are only linked to the nature of the sorbent coating. The coating thickness of CAR–PDMS (75 μm) is much higher than those of PIL-based Fiber C and Fiber D (~7 μm). The calibrations exhibited a linear range with determination coefficients (R) ranging from 0.9914 to 0.9992 for the commercial fiber CAR–PDMS (Table 3), from 0.9938 to 0.9996 for Fiber C (Table 4), and from 0.9939 to 0.9997 for Fiber D (Table 5).

The sensitivity of the HS-SPME method was evaluated by the calibration slope. Higher sensitivities were obtained for phenol+*o*-cresol and 2-ethylphenol, independent of the SPME fiber used. In addition, high sensitivities were also achieved for eugenol and 3-ethylphenol when Fiber C was used, and for 2-heptanone in the case of CAR–PDMS.

The limits of detection (LODs) were calculated as three times the signal to noise ratio. They oscillated between 1.8 μg L^{-1} for *p*-tolualdehyde and 24 μg L^{-1} for heptanoic acid and for octanal, in the case of CAR–PDMS; between 1.6 μg L^{-1} for phenol+*o*-cresol and 78 μg L^{-1} for 2,6-dimethoxyphenol, when Fiber C was used; and from 15.4 μg L^{-1} for 2-ethylphenol to 379 μg L^{-1} for 2,6-dimethoxyphenol, in the case of Fiber D. The obtained LODs are

Table 3
Analytical performance of calibration curves obtained by HS-SPME–GC–FID and the commercial CAR–PDMS fiber.

Analytes	Calibration range (μg L^{-1})	(Slope ± SD[a]) × 10^{-3}	(Intercept ± SD[a]) × 10^{-4}	($S_{y/x}$[b]) × 10^{-4}	R[c]	LOD[d] (μg L^{-1})	n[e]
2-Heptanone	30–1400	1.78 ± 0.06	0.76 ± 4.44	7.8	0.9972	4.8	7
Octanal	100–2000	0.008 ± 0.001	−0.03 ± 0.06	0.07	0.9943	24	5
2-Nonanone	30–2000	0.97 ± 0.05	14.4 ± 5.4	10.1	0.9923	8.5	7
p-Tolualdehyde	30–1400	2.69 ± 0.11	9.46 ± 7.58	14.6	0.9952	1.8	8
Caproic acid	30–2000	0.39 ± 0.02	0.19 ± 1.68	3.1	0.9947	20	7
Guaiacol	30–2000	0.73 ± 0.02	−0.29 ± 1.84	3.8	0.9978	11	8
Heptanoic acid	30–2000	0.55 ± 0.03	1.67 ± 2.57	5.3	0.9914	24	8
Phenol+*o*-cresol	30–2000	1.79 ± 0.04	2.79 ± 3.40	7.0	0.9988	5.8	8
2-Ethylphenol	30–2000	1.45 ± 0.03	7.76 ± 2.50	5.2	0.9988	7.2	8
p-Cresol	30–2000	0.63 ± 0.02	0.17 ± 1.90	3.9	0.9969	16	8
m-Cresol	30–2000	0.68 ± 0.02	0.59 ± 1.93	4.0	0.9972	15	8
Eugenol	30–2000	0.45 ± 0.02	2.83 ± 1.44	3.0	0.9959	8.7	8
3-Ethylphenol	30–2000	0.64 ± 0.01	3.54 ± 1.09	2.0	0.9992	6.1	7
2,6-Dimethoxyphenol	30–2000	0.011 ± 0.001	0.24 ± 0.04	0.08	0.9950	20	9
3-Methoxyphenol	30–2000	0.030 ± 0.001	0.13 ± 0.11	0.24	0.9948	20	7

[a] Standard deviation of the slope and the intercept, for the *n* calibration levels.
[b] Standard deviation of the determination (or error of the estimate).
[c] Correlation coefficient.
[d] Limits of detection, calculated as described in the text.
[e] Calibration levels.

Table 4
Analytical performance of the calibration curves obtained by HS-SPME–GC–FID and the PIL-based coating Fiber C.

Analytes	Calibration range (μg L^{-1})	(Slope ± SD[a]) × 10^{-2}	(Intercept ± SD[a]) × 10^{-4}	($S_{y/x}$[b]) × 10^{-4}	R[c]	LOD[d] (μg L^{-1})	n[e]
p-Tolualdehyde	30–2000	2.26 ± 0.09	−1.31 ± 0.74	1.5	0.9958	20	8
Caproic acid	30–2000	0.97 ± 0.04	−0.27 ± 0.40	0.74	0.9951	16	7
Guaiacol	30–2000	1.67 ± 0.03	−0.56 ± 0.32	0.60	0.9989	9.1	7
Heptanoic acid	60–2000	2.34 ± 0.08	−1.00 ± 0.76	1.4	0.9970	6.5	7
Phenol+*o*-cresol	30–2000	9.26 ± 0.11	−1.08 ± 1.03	1.9	0.9996	1.6	7
2-Ethylphenol	30–2000	8.94 ± 0.13	1.93 ± 1.19	2.2	0.9995	8.7	7
p-Cresol	30–2000	3.78 ± 0.05	−0.43 ± 0.47	0.87	0.9995	21	7
m-Cresol	30–2000	4.58 ± 0.05	−0.20 ± 0.50	0.93	0.9996	17	7
Eugenol	30–2000	5.51 ± 0.14	3.26 ± 1.31	2.4	0.9986	17	6
3-Ethylphenol	30–2000	5.59 ± 0.24	4.45 ± 2.18	4.1	0.9956	17	7
2,6-Dimethoxyphenol	60–1400	0.07 ± 0.01	0.04 ± 0.03	0.05	0.9961	78	5
3-Methoxyphenol	30–2000	0.18 ± 0.01	0.68 ± 0.11	0.17	0.9938	20	6

[a] Standard deviation of the slope and the intercept, for the *n* calibration levels.
[b] Standard deviation of the determination (or error of the estimate).
[c] Correlation coefficient.
[d] Limits of detection, calculated as described in the text.
[e] Calibration levels.

Table 5
Analytical performance of the calibration curves obtained by HS-SPME–GC–FID and the PIL-based coating Fiber D.

Analytes	Calibration range (μg L^{-1})	(Slope ± SD[a])· 10^{-2}	(Intercept ± SD[a])· 10^{-3}	($S_{y/x}$[b])· 10^{-3}	R^2[c]	LOD[d] (μg L^{-1})	n[e]
p-Tolualdehyde	60–3000	0.18 ± 0.01	1.34 ± 0.40	0.78	0.9993	96.0	8
Caproic acid	200–3000	0.10 ± 0.01	−1.42 ± 0.85	1.3	0.9939	134	6
Guaiacol	60–3000	0.17 ± 0.01	−0.52 ± 0.90	1.8	0.9950	81.0	9
Heptanoic acid	500–3000	0.31 ± 0.02	−5.79 ± 3.07	3.7	0.9965	322	5
Phenol + *o*-cresol	30–3000	1.46 ± 0.05	−3.52 ± 6.01	13	0.9962	15.6	10
2-Ethylphenol	30–3000	1.48 ± 0.06	−6.37 ± 6.91	15	0.9958	15.4	8
p-Cresol	60–3000	0.75 ± 0.03	−6.18 ± 4.42	8.6	0.9951	30.4	7
m-Cresol	30–3000	0.97 ± 0.02	−4.25 ± 2.91	6.6	0.9978	23.6	9
Eugenol	500–3000	0.79 ± 0.05	−26.3 ± 8.7	10	0.9955	276	5
3-Ethylphenol	30–2000	0.98 ± 0.02	6.13 ± 0.02	3.7	0.9989	32.4	8
2,6-Dimethoxyphenol	500–3000	0.028 ± 0.001	0.12 ± 0.07	0.09	0.9997	379	5
3-Methoxyphenol	60–3000	0.17 ± 0.01	−1.32 ± 0.90	1.8	0.9952	64.9	7

[a] Standard deviation of the slope and the intercept, for the n calibration levels.
[b] Standard deviation of the determination or error of the estimate.
[c] Correlation coefficient.
[d] Limits of detection, calculated as described in the text.
[e] Calibration levels.

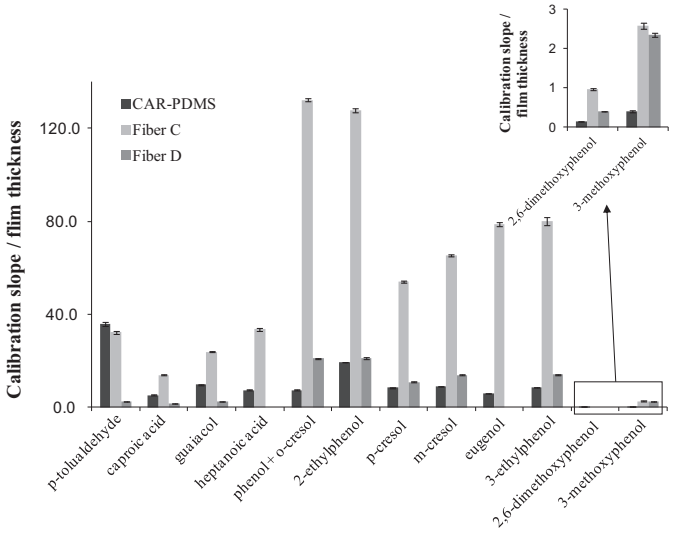

Fig. 2. Normalized slopes (calibration slope/film thickness of SPME fiber) obtained for the analytes studied (except for 2-hepanone, octanal and 2-nonanone) with the proposed HS-SPME–GC–FID method.

satisfactory, especially if considering that FID detection was used in this study. In general, similar LODs values are obtained for Fiber C and CAR–PDMS, and slightly worse for Fiber D. Considering the analyte, lower LOD values were obtained for aldehydes and ketones when using the CAR–PDMS fiber. For free fatty acids, lower LOD values were obtained with Fiber C.

The reproducibility of the method was evaluated by performing intra-day and inter-day experiments. Intra-day ($n=3$) precision was estimated by measuring working solutions at two concentration levels: all analytes at 500 μg L^{-1} (spiked level 1), and a higher level with a concentration of: 2.5 mg L^{-1} for 2-heptanone and 2-nonanone, 5.0 mg L^{-1} for *p*-tolualdehyde, heptanoic acid, phenol, *o*-cresol and eugenol, 7.0 mg L^{-1} for octanal, caproic acid, guaiacol, 2-ethylphenol, *p*-cresol and 3-ethylphenol, 10.0 mg L^{-1} for *m*-cresol and 3-methoxyphenol, and 12.0 mg L^{-1} for 2,6-dimethoxyphenol (spiked level 2). The obtained results are shown in Table 6. For the spiked level 1, relative standard deviations (RSD in %) ranged from 3.4 to 21% for CAR–PDMS, from 3.8 to 19% for Fiber C, and from 1.8 to 22% for Fiber D, and therefore being quite similar for all SPME fibers.

With regards to inter-day precision ($n=6$), it was determined in two non-consecutive days using the spiked level 1. RSDs values are also shown in Table 6. They ranged from 2.3 to 22% for CAR–PDMS, from 6.1 to 20% for Fiber C, and from 5.2 to 23% for Fiber D. It must be highlighted that these values are totally acceptable, particularly since the HS-SPME method was performed without an autosampler. Precision data for PIL-based coatings Fiber A and Fiber B have been included in Table S5 of the Supplementary materials. Again, there are not important differences among SPME fibers. Furthermore, there are not significant differences among the intra-day and inter-day variances for each analyte with each of the PIL-based SPME fibers studied, as confirmed by the analysis of variance (ANOVA) test (Table S6 of Supplementary materials).

Cheese samples were extracted using PIL-based sorbent coatings obtained by UV polymerization and the proposed HS-SPME–GC–FID method, to evaluate the performance of the fibers with real samples rather than with standards. Representative chromatograms are shown in Fig. 3.

Guaiacol, 2-ethylphenol, *p*-cresol and *m*-cresol were not detected in the cheese sample with any SPME fiber. 2-Heptanone, octanal and 2-nonanone were only detected with the commercial CAR–PDMS fiber. The remaining studied analytes were detected with all SPME fibers, with identical peak symmetry. From Fig. 3, it is clear that higher extraction efficiency was obtained for Fiber C compared to Fiber D.

3.5. Extraction efficiency evaluated as normalized calibration slope

It is well known that the extraction efficiency of SPME fibers mainly depends on three parameters: the nature, the film thickness, and the surface area of the extraction phase of the coating, provided that the experimental variables of the particular experiment remain constant [36–38].

In this study, all SPME fibers (commercial CAR–PDMS and PIL-based sorbent coatings) possess the same length (1 cm). Although their surface area cannot be assumed as equal, we can consider them as similar, simply as a helpful approximation.

In any case, the nature and the film thickness are different for each SPME fiber (see Table 1), ranging from 75 μm for CAR–PDMS to ~7 μm for Fiber C and Fiber D. On average, CAR–PDMS is ~11 times thicker than Fibers C and D. Thus, extraction efficiencies are not only due to the nature of the coating but to the coating thickness.

It has been proposed to compare the extraction efficiency of SPME fibers possessing different coatings and thickness by means of the normalized slope [23,25]. The normalized slope is obtained by dividing the calibration slope of a SPME method (HS-SPME–

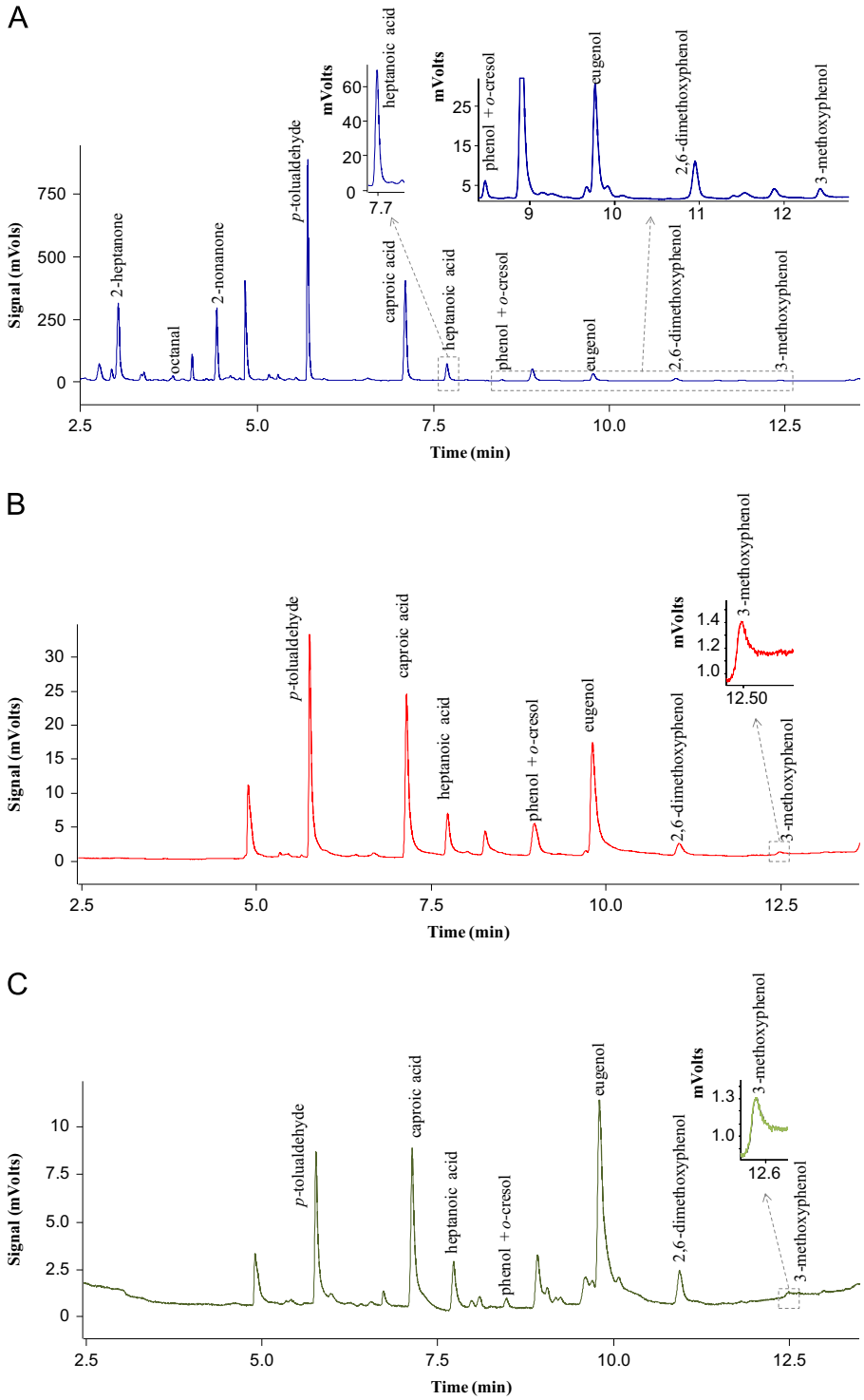

Fig. 3. Chromatograms obtained analyzing cheese samples and the HS-SPME–GC–FID method with (A) CAR–PDMS fiber, (B) PIL-based Fiber C, and (C) PIL-based Fiber D.

GC–FID method in this particular case) for a particular analyte by the coating thickness of the SPME fiber used. In this approach, the normalized slope permits comparisons to be established which only focus on the nature of the fiber coating. The normalized slopes obtained for the crosslinked PIL coatings (Fiber C and Fiber D) and the commercial CAR–PDMS fiber have been included in Fig. 2. The volatile analytes 2-heptanone, octanal and 2-nonanone were excluded in this comparison because they were only extracted with CAR–PDMS.

The obtained values of the normalized slopes oscillate between 0.11 ± 0.01 for octanal and 35.9 ± 1.4 for *p*-tolualdehyde using CAR–PDMS; between 0.96 ± 0.06 for 2,6-dimethoxyphenol and 132 ± 2 for phenol+*o*-cresol using Fiber C; and between 0.40 ± 0.01 for 2,6-dimethoxyphenol and 21.1 ± 0.8 for phenol+*o*-cresol when using Fiber D. These results show that the highest normalized slopes are obtained with Fiber C, except for *p*-tolualdehyde, which presented similar values to that of CAR–PDMS. This is in agreement with the obtained log K_{fs} values. In addition, Fiber D presents higher normalized slopes than CAR–PDMS for the majority of phenols (except for guaiacol). In general, it can be concluded that the crosslinked PIL-based sorbent coatings are more effective than

Table 6
Repeatability (RSD intra-day) and reproducibility (RSD inter-day) for CAR–PDMS and PIL-based coatings Fiber C and Fiber D.

Analyte	RSD intra-day[a] (%), spiked level 1[b]			RSD intra-day[a] (%), spiked level 2[c]			RSD inter-day[d] (%), spiked level 1[b]		
	CAR–PDMS	Fiber C	Fiber D	CAR–PDMS	Fiber C	Fiber D	CAR–PDMS	Fiber C	Fiber D
2-Heptanone	3.4	nd[e]	nd[e]	13	nd[e]	nd[e]	3.4	nd[e]	nd[e]
Octanal	12	nd[e]	nd[e]	21	nd[e]	nd[e]	8.8	nd[e]	nd[e]
2-Nonanone	6.4	nd[e]	nd[e]	9.5	8.7	15	20	nd[e]	nd[e]
p-Tolualdehyde	4.0	7.5	7.5	17	19	19	6.0	20	23
Caproic acid	18	10	10	10	17	24	2.3	8.5	14
Guaiacol	15	3.8	1.8	7.3	4.8	19	6.0	11	5.2
Heptanoic acid	17	7.6	8.2	13	8.0	13	2.8	6.4	23
Phenol+*o*-cresol	12	5.7	22	4.6	3.3	11	7.7	6.1	23
2-Ethylphenol	13	7.5	5.7	9.0	5.1	5.9	4.3	8.5	22
p-Cresol	14	7.7	13	4.0	5.8	12	8.2	8.4	12
m-Cresol	14	6.4	13	2.6	6.0	8.8	9.0	7.1	13
Eugenol	21	5.5	20	10	10	16	14	7.7	17
3-Ethylphenol	14	5.4	5.4	1.4	2.4	15	7.1	9.4	15
2,6-Dimethoxyphenol	6.0	19	7.7	19	9.2	17	5.5	18	11
3-Methoxyphenol	19	10	4.4	16	10	18	22	11	12

[a] Relative standard deviation ($n=3$).
[b] Spiked level of 500 $\mu g\,L^{-1}$ for each analyte.
[c] Spiked level with a concentration of: 2.5 $mg\,L^{-1}$ for 2-heptanone and 2-nonanone, 5.0 $mg\,L^{-1}$ for *p*-tolualdehyde, heptanoic acid, phenol, *o*-cresol and eugenol, 7.0 $mg\,L^{-1}$ for octanal, caproic acid, guaiacol, 2-ethylphenol, *p*-cresol and 3-ethylphenol, 10.0 $mg\,L^{-1}$ for *m*-cresol and 3-methoxyphenol, and 12.0 $mg\,L^{-1}$ for 2,6-dimethoxyphenol.
[d] Relative standard deviation, calculated in 2 non-consecutive days ($n=6$).
[e] Not determined for reasons detailed in the text.

CAR–PDMS, and evidently more effective than other commercial SPME fibers, in the extraction of the selected group of volatile compounds.

4. Conclusions

PIL-based SPME coatings have shown to be quite efficient materials for the headspace extraction of volatiles from cheeses, especially crosslinked PIL-based coatings obtained by UV-polymerization. The performance of these materials has been compared with commercial SPME coatings, with CAR–PDMS being the most successful commercial fiber for these analytes.

Among the four PIL-based coatings studied, the coatings produced by UV polymerization and containing the IL monomer 1-vinyl-3-hexylimidazolium chloride, and 1,12-di(3-vinylimidazolium)dodecane dibromide as crosslinker, demonstrated superior performance for the extraction of the selected analytes from cheeses. With regards to the comparison of the partition coefficients from the sample to the fibers (K_{fs}) for those analytes characterized with all fibers, this PIL-based fiber generally presented higher values. The log K_{fs} values, estimated only as an approximation, oscillated between 1.25 ± 0.08 for 2,6-dimethoxyphenol and 1.96 ± 0.03 for eugenol. The normalized calibration slope (obtained from the ratio calibration slope to coating thickness) is a quite simple tool to compare among coatings nature, and the conclusions derived from it are totally similar to those obtained with K_{fs} values. Thus, highest normalized slopes are obtained with this PIL-based fiber, except for *p*-tolualdehyde, which presented similar values to that of CAR–PDMS.

Ongoing work is aimed to modify the polymerization strategy to obtain thicker PIL-based coatings.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.12.046.

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