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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-polydimethylsiloxane (CAR-PDMS). For the PIL-based fibers, the highest  $K_{fs}$  value ( $1.96 \pm 0.03$ ) 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-vinylimidazolium)dodecane dibromide IL crosslinker exhibited the best performance in the extraction of the select analytes from cheeses. Despite a coating thickness of only 7  $\mu\text{m}$ , this copolymeric sorbent coating was capable of quantitating analytes in HS-SPME in a 30 to 2000  $\mu\text{g L}^{-1}$  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  $\mu\text{g L}^{-1}$ .

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## 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  $\times$  GC) [7].

The primary commercial SPME coatings employed in the monitoring of volatile compounds in cheeses include carboxen-polydimethylsiloxane (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 polydimethylsiloxane (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 (≥ 98.0%), 2,6-dimethoxyphenol or syringol (≥ 97%) and 3-methoxyphenol (≥ 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 (≥ 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<sup>-1</sup>, being of 973 mg L<sup>-1</sup> for octanal.

These individual solutions were used to prepare a working solution containing 2.5 mg L<sup>-1</sup> of 2-heptanone and 2-nonanone; 5.0 mg L<sup>-1</sup> of heptanoic acid, *p*-tolualdehyde, phenol, *o*-cresol and eugenol; 7.0 mg L<sup>-1</sup> of caproic acid, octanal, *p*-cresol, 2-ethylphenol, 3-ethylphenol and guaiacol; 10.0 mg L<sup>-1</sup> of *m*-cresol and 3-methoxyphenol; and 12.0 mg L<sup>-1</sup> 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<sup>-1</sup> in acetonitrile. HS-SPME calibration working solutions (between 30 and 3000 μg L<sup>-1</sup>) 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<sup>-1</sup> for caproic acid, 2888 mg L<sup>-1</sup> for heptanoic acid, 2000 mg L<sup>-1</sup> 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<sup>-1</sup> for 2-ethylphenol and 3-ethylphenol, and 973 mg L<sup>-1</sup> 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<sup>-1</sup>.

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<sup>2</sup> 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<sub>2</sub>) 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,

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