Talanta 200 (2019) 415–423

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Zwitterionic polymeric ionic liquid-based sorbent coatings in solid phase microextraction for the determination of short chain free fatty acids

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ARTICLE INFO

Keywords:
Polymeric ionic liquids
Zwitterionic liquid
Solid-phase microextraction
Short chain free fatty acids
Wine

ABSTRACT

Five different zwitterionic sorbent coatings based on polymeric ionic liquids (PILs) were developed by the *on fiber* UV co-polymerization of the zwitterionic monomers 1-vinyl-3-(alkylsulfonate)imidazolium or 1-vinyl-3-(alkylcarboxylate)imidazolium and different dicationic ionic liquid (IL) crosslinkers. The developed sorbent coatings were applied in headspace solid-phase microextraction in combination with gas chromatography-mass spectrometry for the determination of short chain free fatty acids in wine. The sorbent coatings were found to extract these analytes via a non-competitive extraction mechanism. The methodology was optimized for the two best zwitterionic PIL coatings and compared to the commercially-available carboxen/polydimethylsiloxane (CAR/PDMS) and polyacrylate (PA) fibers. The sorbent coating based on the 1-vinyl-3-(propanesulfonate)imidazolium IL (Fiber **1**) was more sensitive than PA while providing similar limits of detection to CAR/PDMS for the determination of analytes in a diluted synthetic wine sample. At the same time, Fiber **1** required lower extraction times (only 20 min versus 60 min for CAR/PDMS and 40 min for PA), exhibited higher reproducibility (with relative standard deviation lower than 8.9% for a spiked level of 7 μM) and was more tolerant to ethanol present within the sample. The zwitterionic PILs were also applied for the analysis of red wine, and the results were in agreement with those obtained for CAR/PDMS. The analytes were detected and quantified in the concentration range from 0.18 ± 0.03 mg L^{-1} to 4.8 ± 0.9 mg L^{-1}, depending on the analyte and fiber.

1. Introduction

Polymeric ionic liquids (PILs) are a subclass of polyelectrolytes prepared by the polymerization of ionic liquid (IL) monomers [1]. PILs possess low-to-negligible vapor pressure at room temperature, high chemical and mechanical stability as well as impressive structural tunability, allowing for the preparation of task-specific materials by tailoring the chemical composition. Moreover, they often provide higher thermal stability and viscosity compared to ILs, properties that are derived from their polymeric nature. These aforementioned properties make PILs attractive materials for a number of applications within different scientific fields [2].

PILs are classified as polycations, polyanions or polyzwitterions based on the repeating electrolyte unit within the PIL backbone [1]. Zwitterionic PILs have garnered attention in the last several years [1,3,4]. These polymers are composed of both cations and anions covalently linked as a repeating unit within the polymer backbone. The presence of closely and oppositely charged moieties within the polymer structure has led to interesting materials that exhibit high dipole moments while maintaining charge neutrality [3,5]. In addition, they possess a wide chemical diversity due to the possibility of combining different cations (e.g., ammonium [6], imidazolium [5,7] or phosphonium [5]) and anions (e.g., sulfonate [7] or carboxylate [7,8]), and the feasibility of modulating the proximity of these positive and negative charges [3].

Within analytical chemistry, PILs have been particularly successful as sorbent coatings in solid-phase microextraction (SPME) [9,10]. SPME is a non-exhaustive extraction and preconcentration method based on the partitioning of analytes from the sample to a small amount of sorbent phase typically coated on a solid fiber support [12]. The success of this technique in environmental, biological and food analysis lies with its simplicity, environmental-friendliness, ease of automation,

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https://doi.org/10.1016/j.talanta.2019.03.073
Received 14 February 2019; Received in revised form 16 March 2019; Accepted 18 March 2019
Available online 19 March 2019
0039-9140/

and high enrichment factors. However, for a number of analytes and sample matrices current commercially-available coatings lack selectivity [11]. PIL-based sorbent coatings, due to their wide solvation capabilities, can overcome some limitations of commercial fibers [9,13].

A high number of PIL-based SPME sorbent coatings are based on the co-polymerization of two different ILs, generally a monocationic IL monomer and a dicationic IL crosslinker [14–16]. Moreover, taking advantage of the synthetic versatility of these materials, a large variety of PIL coatings have been developed [13]. Double-confined PILs have been prepared by employing ILs containing polymerizable moieties in both the cation and anion with the objective of enhancing the mechanical stability of the coatings to yield matrix-compatible coatings [17]. IL monomers have also been functionalized to include specific groups in their chemical structures. PIL-based coatings containing halide anions or polar substituents in the cationic moiety have been demonstrated to be more efficient in the extraction of polar compounds [14,18], while those with vinylbenzyl groups within the cation provided better results for aromatic compounds [19,20]. Crosslinked PIL-based sorbent coatings with carboxylic groups in the cationic moiety have also been developed for the selective extraction of DNA [21], while PILs containing cations with unique structural motifs have demonstrated increased sensitivity for the extraction of acrylamide [22]. More recently, the incorporation of silver ions within the IL monomer was reported, leading to the preparation of coatings with unique selectivity towards alkenes and alkynes [23]. However, to the best of our knowledge, zwitterionic PILs have never been applied in SPME.

The determination of volatile compounds in foods and beverages is important since their concentration affects sensory properties and often determines the quality of the product [24]. Volatile short chain free fatty acids (SCFFAs) are among the main compounds that contribute to the aroma of fermented products, while also being responsible for various characteristic flavors and off-flavors in dairy products and alcoholic fermented beverages [25–27]. Headspace (HS-) SPME has been explored in these applications [25,28–30]. Adsorption-type commercial fibers such as carboxen/polydimethylsiloxane (CAR/PDMS) and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) have generally been used over absorption-type coatings given their higher sensitivity. However, a large number of interferences are generally extracted from samples together with target analytes, which makes the analysis of real samples very challenging [30]. Therefore, the development of sorbent coatings able to selectively extract specific groups of compounds without being affected by the presence of interfering substances is of particular interest when analyzing complex matrixes with SPME. In the case of alcoholic beverage analysis, the use of sorbent coatings that are not affected by the alcohol content of the sample is of special interest [30].

In this study, PIL-based sorbent coatings comprised of zwitterionic IL monomers and dicationic IL crosslinkers were developed for the first time and their unique selectivity examined. The prepared fibers were assessed in HS-SPME for the extraction of SCFFAs and their primary extraction mechanism was determined. The analytical performance of the zwitterionic PIL fibers, in combination with gas chromatography-mass spectrometry (GC-MS), was evaluated in synthetic and real wine samples. The influence of ethanol content within the sample on the extraction efficiency of the method was studied for these sorbent coatings. Moreover, the proposed methodology was compared with suitable commercial fibers for the application.

2. Experimental

2.1. Chemicals, reagents, materials and samples

The SCFFA certified reference material CRM46975 used as standard mix was purchased from Supelco (Bellefonte, PA, USA). The certified material was a multi-component aqueous solution that contained propionic acid (C_3), *iso*-butyric acid (*i*-C_4), *n*-butyric acid (*n*-C_4), *iso*-valeric acid (*i*-C_5), *n*-valeric acid (*n*-C_5), *iso*-hexanoic acid (*i*-C_6), *n*-hexanoic acid (*n*-C_6), and *n*-heptanoic acid (*n*-C_7) each at 10 mmol L^{-1}. An intermediate standard solution of the SCFFAs at 2 mmol L^{-1} was prepared by dilution of the certified material with ultrapure water. Working solutions were prepared by spiking a certain volume of either the standard mix or the intermediate standard solution in ultrapure water, diluted synthetic wine, or diluted wine sample. Ultrapure water (18.2 MΩ cm) was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA), while NaCl (≥99.5%) was purchased from Fisher Scientific (Fair Lawn, NJ, USA).

For the preparation of zwitterionic PIL sorbent coatings, elastic nitinol wires with an external diameter of 127 mm from Nitinol Devices & Components (Fermont, CA, USA) were used as solid supports, while blank SPME assemblies (24 Ga) were provided by Millipore-Sigma (Bellefonte, PA, USA). Functionalization of the nitinol wires required hydrogen peroxide (30%, w/w) purchased from Fisher Scientific, and vinyltrimethoxysilane (VTMS) obtained from Sigma-Aldrich. The radical initiator 2-hydroxy-2-methylpropiophenone (> 96.0%, DAROCUR 1173) was supplied by Sigma-Aldrich and used for the co-polymerization of the ILs. The commercial polyacrylate (PA, 85 μm film thickness) and carboxen/polydimethylsiloxane (CAR/PDMS, 75 μm film thickness) sorbent coatings were supplied as gifts from Millipore-Sigma.

Synthetic wine was prepared according to previously published methods [31,32] using an aqueous solution of 3.5 g L^{-1} of (+)-tartaric acid (Sigma-Aldrich) containing 13% (v/v) of ethanol (Sigma-Aldrich), and adjusting the pH to 3.5 with 1 M NaOH (Fisher Scientific). Red wine (Pinot noir 2014, with 13%, v/v, ethanol content) was purchased from a local store in Ames, IA, USA.

2.2. Instrumentation

An Agilent Technologies (Santa Clara, CA, USA) model 7890B GC equipped with 5977A MS detector (single quadrupole) was used for the separation and detection of the SCFFAs. Ultrapure helium was used as carrier gas at a flow rate of 1 mL min^{-1}. The inlet was operated in *splitless* mode at different temperatures depending on the SPME fiber: 175 °C or 200 °C for the zwitterionic PIL sorbent coatings, 280 °C for PA and 290 °C for CAR/PDMS. A HP-FFAP capillary column (30 m × 0.25 mm I.D. × 25 μm film thickness) from Agilent Technologies was used for the separation of analytes. The following temperature oven program was employed: 2 min at 80 °C, then the temperature was increased to 100 °C at 25 °C min^{-1}, followed by an increase at 10 °C min^{-1} up to 240 °C, and finally held for 2 min. The MS employed electron ionization (EI) at 70 eV and was used in gain factor mode. The transfer line temperature was set at 250 °C, while the source and quadrupole temperatures were fixed at 230 °C and 150 °C, respectively. Data was acquired in single ion monitoring (SIM) mode using the segment program shown in Table S1 of the Supplementary Material (SM). Identification of the SCFFAs was accomplished considering the retention time, the presence of quantifier and qualifier ions for each analyte, and the ratio between those ions. The peak area of the quantifier ion was used for the quantification of the compounds.

Scanning electron microscopy (SEM) images of the fibers were acquired in a FEI Quanta-250 microscope and were used for the estimation of sorbent coating film thickness.

2.3. Procedures

2.3.1. Preparation of zwitterionic PIL fibers

Five different zwitterionic PIL sorbent coatings were prepared combining different zwitterionic IL (ZIL) monomers and IL crosslinkers, as shown in Table 1.

The ZIL monomers and IL crosslinkers, whose structures are shown in Fig. S1 of the SM, were synthesized according to procedures detailed

Table 1
Composition and maximum operating temperature of the developed zwitterionic PIL sorbent coatings.

Zwitterionic PIL	ZIL monomer	IL crosslinker[a]	Maximum operating temperature (°C)
Fiber **1**	[VIm$^+$C$_3$SO$_3^-$][b]	[(VIm)$_2$C$_{12}^{2+}$]2[Br$^-$][c]	175
Fiber **2**	[VIm$^+$C$_3$SO$_3^-$][b]	[(VIm)$_2$C$_{12}^{2+}$]2[NTf$_2^-$][d]	200
Fiber **3**	[VIm$^+$C$_4$SO$_3^-$][e]	[(VIm)$_2$C$_{12}^{2+}$]2[Br$^-$][c]	175
Fiber **4**	[VIm$^+$C$_9$COO$^-$][f]	[(VIm)$_2$C$_{12}^{2+}$]2[Br$^-$][c]	175
Fiber **5**	[VIm$^+$C$_9$COO$^-$][f]	[(VIm)$_2$C$_{12}^{2+}$]2[NTf$_2^-$][d]	200

*The structures of all ZILs and ILs used in this study are shown in Fig. S1 of the SM.
[a] 1:1 mass ratio (monomer: crosslinker).
[b] 1-Vinyl-3-(propanesulfonate)imidazolium.
[c] 1,12-Di(3-vinylimidazolium)dodecane bromide.
[d] 1,12-Di(3-vinylimidazolium)dodecane bis[(trifluoromethyl)sulfonyl]imide.
[e] 1-Vinyl-3-(butanesulfonate)imidazolium.
[f] 1-Vinyl-3-(nonanocarboxylate)imidazolium.

within the SM following previously described methods [8,33–35]. The ZIL monomers were prepared by ring-opening of the appropriate alkysultone by 1-vinylimidazole, or by reacting 1-vinylimidazole with the appropriate bromo-substituted alkylcarboxylic acid followed by ion exchange with hydroxide and successive neutralization between the hydroxide and the carboxylic acid.

Zwitterionic PIL sorbent coatings were prepared by *on fiber* UV co-polymerization using DAROCUR 1173 as a free radical initiator [14]. Prior to polymerization, the nitinol wire used as solid support was functionalized according to a previously reported method [36]. Briefly, the wires were immersed in hydrogen peroxide (30%, w/w) to impart hydroxyl groups on the surface. The nitinol wires were then treated with VTMS to functionalize the surface with vinyl moieties that facilitate anchoring the PIL to the solid support. The derivatized nitinol wires were then glued onto a commercial blank SPME assembly and 1.3 cm were exposed for its coating. The co-polymerization was accomplished using a mixture consisting of the ZIL monomer and IL crosslinker (at a mass ratio of 1:1) together with DAROCUR 1173 (5% w/w respect to the ZIL monomer). The mixture was placed on the surface of the functionalized nitinol and the fibers were exposed to UV irradiation using a RPR-100 reactor with a spinning carousel (Southern New England Ultraviolet Company, Bradford, CT, USA). Co-polymerization was carried out at 254 nm for 2 h in the case of the zwitterionic PILs containing the bromide-based crosslinker, or at 360 nm for 2 h for sorbent coatings containing the [NTf$_2^-$]-based crosslinker. Finally, the zwitterionic PIL sorbent coatings were conditioned in the GC inlet for 30 min at 175 °C for Fibers **1**, **3** and **4**, and at 200 °C for the remaining fibers.

2.3.2. Headspace solid-phase microextraction

HS-SPME extractions were performed in 20 mL amber glass vials with screw caps and polytetrafluoroethylene/silicon septa (Supelco) using magnetic stir bars of 1 cm length × 0.5 cm diameter (Fisher Scientific). For the optimization of the methodology, 10 mL of aqueous solution containing 0–30% (w/v) of NaCl and the SCFFAs at concentrations between 1.6 and 2.7 mg L^{-1}, depending on the analyte, were placed in the vial and the stirring rate was fixed at 600 rpm. The fiber was exposed to the headspace of the solution for 20–80 min at 35–65 °C. After extraction, the SCFFAs were thermally desorbed in the GC inlet for 2–10 min at 175 °C for Fibers **1**, **3**, and **4**, 200 °C for Fibers **2** and **5**, 280 °C for PA, and 290 °C for CAR/PDMS. Optimum conditions for the HS-SPME-GC-MS method are listed in Table 2.

The analytical performance of the method in ultrapure water was determined under optimum conditions with spiked concentrations of the analytes ranging from 7·10^{-4} to 13 mg L^{-1}. To evaluate the effect of ethanol content on extraction efficiency, 10 mL of aqueous solution containing 30% (w/v) of NaCl and 1.3% (v/v) of ethanol were prepared and the analytes were spiked at concentrations ranging from 0.5 to 0.9 mg L^{-1}, depending on the SCFFA. Then, the HS-SPME-GC-MS method was applied under the optimum conditions (Table 2).

Table 2
Optimum conditions for the HS-SPME-GC-MS method using different fibers.

Parameter	Fiber 1	Fiber 4	CAR-PDMS	PA
Total sample volume	10 mL	10 mL	10 mL	10 mL
NaCl concentration	30% (w/v)	30% (w/v)	30% (w/v)	30% (w/v)
Extraction temperature	65 °C	65 °C	65 °C	65 °C
Extraction stirring	600 rpm	600 rpm	600 rpm	600 rpm
Extraction time	20 min	60 min	60 min	40 min
Desorption temperature	175 °C	175 °C	290 °C	280 °C
Desorption time	4 min	2 min	2 min	4 min

For the analysis of synthetic or red wine, 1 mL of sample was added to 9 mL of ultrapure water and the NaCl content was adjusted to 30% (w/v). A pH value of 3 was used for the diluted samples. Analytes were spiked at concentrations varying between 0 and 13 mg L^{-1}, depending on the experiment. HS-SPME-GC-MS experiments were performed at the optimum conditions detailed in Table 2. Blank extractions using ultrapure water were performed between samples during the analysis of red wine to avoid *carry over*.

The extraction mechanism of Fibers **1** and **4** was evaluated according to previously reported methods [15,23]. The SCFFAs *i*-C$_4$ and *n*-C$_7$ were selected as the target sorbate and interfering compound, respectively. A volume of 1 mL of synthetic wine was added to 9 mL of ultrapure water, and the NaCl content was adjusted to 30% (w/v). HS-SPME experiments were performed using optimum conditions (Table 2). Calibration curves of *i*-C$_4$ in the range between 0.2 and 30 mg L^{-1} were constructed in the presence of two relative concentrations of *n*-C$_7$ with respect to *i*-C$_4$ (i.e., 1:1 or 1:10 ratio – *i*-C$_4$: *n*-C$_7$ ratio).

3. Results and discussion

3.1. Screening of different zwitterionic PIL fibers

As a preliminary study, the prepared zwitterionic PIL sorbent coatings (Table 1) were screened for the determination of SCFFAs together with the commercial CAR/PDMS fiber, which has been previously reported as one of the most suitable SPME fibers for these compounds [28,29]. Extractions were performed from an aqueous solution containing 20% (w/v) of NaCl at 45 °C for 20 min, followed by thermal desorption for 6 min.

Fig. 1 shows the extraction efficiency expressed as the chromatographic peak area for each analyte and fiber. Fibers **4** and **5**, containing the [VIm$^+$C$_9$COO$^-$] ZIL monomer, provided similar or better results than the commercial CAR/PDMS fiber for all analytes. When the fibers containing sulfonate-based ZIL monomers were compared, Fibers **1** and **2** (containing [VIm$^+$C$_3$SO$_3^-$]) yielded slightly higher peak areas than Fiber **3** (with the [VIm$^+$C$_4$SO$_3^-$] monomer). This result seems to

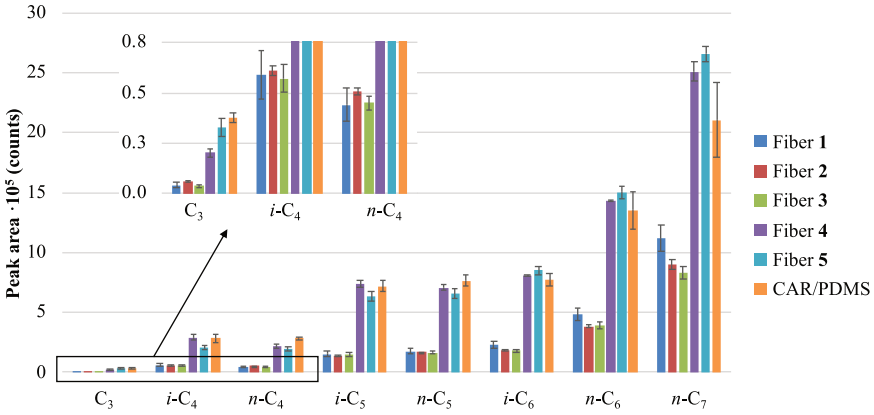

Fig. 1. Extraction efficiency, expressed as chromatographic peak area, obtained for the SCFFAs after performing HS-SPME-GC-MS using zwitterionic PIL and CAR/PDMS sorbent coatings. Experimental conditions (n = 3): 10 mL of aqueous solution containing the SCFFAs at 0.02 mmol L^{-1}; 20% (w/v) of NaCl; 20 min of extraction at 45 °C and 600 rpm; desorption for 6 min at 175 °C for Fibers **1**, **3** and **4**, 200 °C for Fibers **2** and **5**, and 290 °C for CAR/PDMS.

indicate that the length of the alkyl chain of the ZIL monomer may not have an important effect on the extraction efficiency. With regard to the crosslinker, there were generally no significant differences observed between fibers with the same monomer and different crosslinker. However, the results obtained with fibers containing the bromide-based crosslinker were slightly better for longer alkyl chain SCFFAs with the [$VIm^+C_3SO_3^-$]-based sorbent coating (Fiber **1**) compared to Fiber **2**, and for smaller SCFFAs using Fiber **4** rather than Fiber **5**. These results may be related to the relatively higher hydrogen-bond basicity of the sorbent coatings containing bromide anions with respect to coatings containing the [NTf_2^-] anion, which can promote additional strong interactions with the analytes [37,38]. Based on the results, Fiber **1** and Fiber **4** were selected for the development of the HS-SPME-GC-MS method for the determination of SCFFAs.

3.2. Extraction mechanism of the zwitterionic PIL fibers

The primary extraction mechanism (i.e., absorption or adsorption) exhibited by the zwitterionic PIL Fibers **1** and **4** was evaluated by performing a previously reported approach [15,23]. The method consists of developing calibration curves of a target sorbate in the presence of an interfering compound at two different relative concentration levels. If adsorption is the primary extraction mechanism, both the sorbate and the interfering compound can compete for the limited available sorption sites of the coating. The concentration of the sorbate in this particular case can be affected under equilibrium conditions, especially for analytes with lower affinity to the sorbent coating [23,39]. Therefore, an increase in the concentration of the interfering compound can cause a change of the sensitivity of the target analyte [39].

In absorptive-type extractions, diffusion of the analytes through the sorbent coating is a dominant effect [11]. Therefore, analytes can freely partition into the sorbent, with little competition among analytes, and the concentration of each analyte at equilibrium is less affected by the presence of other analytes.

In this approach, calibration curves of *i*-C_4 (as target sorbate) were constructed in the presence of two relative concentrations of *n*-C_7, acting as interfering compound. The two relative concentration ratios were denoted as 1:1 and 1:10 (*i*-C_4: *n*-C_7 ratio). The obtained curves are shown in Fig. 2. Both fibers exhibited similar behavior and no differences were observed for the curves of *i*-C_4 when different relative concentrations of the interfering compound, *n*-C_7, were present in the extraction vial. These results were confirmed by the analysis of the corresponding linear segments of the curves, as Table S2 of the SM shows. For Fiber **1**, the obtained slopes in the linear range 0.5–16 mg L^{-1} were $(2.5 \pm 0.2)\cdot10^{-4}$ and $(2.9 \pm 0.2)\cdot10^{-4}$ for calibrations employing 1:1 and 1:10 ratios, respectively, and the standard deviation of the residuals was $2.1\cdot10^{-4}$ in both cases. Statistical analysis revealed equal slope variances and no significant differences between the slopes (95% confidential level, statistical test according to [40]). With regard to Fiber **4**, the results indicated different slope variances but no significant differences between the slopes (see Table S2). The obtained data also revealed that the sensitivity of the fibers towards the extraction of *i*-C_4 was not affected by the presence of *n*-C_7. Therefore, it can be concluded that absorption is the primary extraction mechanism of the studied zwitterionic PILs. This behavior is similar to the commercially-available PA and PDMS fibers, and different than that observed for CAR/PDMS for which a competitive extraction mechanism is typical [11,15,23].

This approach was previously applied for studying the primary extraction mechanism of both linear and crosslinked PIL-based sorbent coatings [15,23]. The studies performed with sorbent coatings based on monocationic IL monomers revealed an absorption-type extraction mechanism [15]. However, sorbent coatings generated with silver-based IL monomers demonstrated primarily an adsorptive-type extraction mechanism [23]. Therefore, it can be concluded that PILs can be

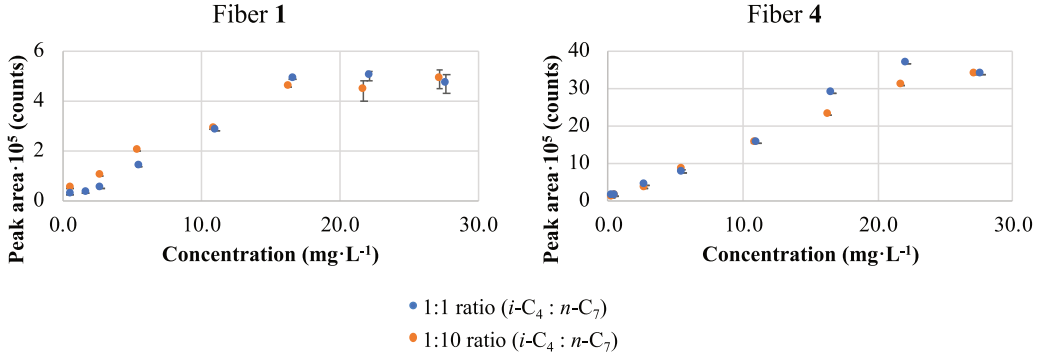

Fig. 2. Calibration curves of *i*-C_4 in the presence of two *i*-C_4: *n*-C_7 concentration ratios (1:1 or 1:10) for Fibers **1** and **4**. Experiments were performed in dilute synthetic wine using optimum conditions summarized in Table 2.

chemically tuned to extract analytes via absorption- or adsorption-type mechanisms by simple changes of the composition of the IL monomer.

3.3. Optimization of the method with commercial and zwitterionic PIL fibers

The HS-SPME procedure was optimized following a factor-by-factor approach for the zwitterionic PILs (Fibers **1** and **4**), together with the commercial CAR/PDMS and PA fibers for comparison purposes. CAR/PDMS was selected as it has been previously used in the determination of SCFFAs [28,29]. Given the polarity of the analytes, the PA fiber was also included in the study as a representative fiber with an absorptive-type extraction mechanism [15].

Experimental parameters affecting HS-SPME were previously fixed to ensure high extraction efficiency and adequate sensitivity, such as 10 mL of sample volume, 600 rpm of stirring rate and the desorption temperature at the maximum operational temperature for each fiber (175 °C for zwitterionic PIL-based fibers, 280 °C for PA, and 290 °C for CAR/PDMS). The main parameters influencing HS-SPME, including the ionic strength (evaluated as NaCl content), extraction temperature, extraction time and desorption time, were optimized.

3.3.1. Effect of NaCl content

In HS-SPME, the extraction efficiency can be improved by the addition of a salting-out agent in order to reduce the solubility of the analytes, effectively increasing the concentration of analytes in the headspace [25]. Therefore, the effect of the NaCl concentration was evaluated from 0% to 30% (w/v) for the zwitterionic PIL sorbent coatings. Fig. S2 of the SM includes the peak areas obtained for each SCFFA examined. Extractions were performed at 45 °C for 20 min followed by desorption for 6 min. As expected, the higher NaCl concentration resulted in higher amounts of analyte extracted with the best results using 30% (w/v). It is interesting to mention the sharper enhancement in extraction efficiency obtained for Fiber **1** compared with Fiber **4**, which leads to similar peak areas using both zwitterionic PIL-based fibers for all the SCFFAs. Taking into account this general tendency, 30% (w/v) NaCl was selected as optimum for both PIL-based and commercial fibers.

3.3.2. Effect of temperature

The temperature during extraction in HS-SPME plays an important role in the amount of analyte extracted since higher temperatures improve the transfer of analytes from the sample to the headspace [11]. However, relatively high temperatures can be detrimental as they can reduce the partition coefficients of the analytes to the sorbent coating. The extraction temperature was evaluated between 35 and 65 °C for 20 min using 30% (w/v) of NaCl and a desorption time of 6 min. Fig. S3 of the SM shows similar behavior for both Fiber **1** and Fiber **4** with the extraction efficiency increasing as the temperature was increased. In these cases, the relatively high temperatures did not reduce the partitioning of the analytes due to the strong interaction between the zwitterionic PILs and the SCFFAs. Given these results, 65 °C was selected for subsequent experiments using all studied fibers.

3.3.3. Effect of extraction time

The extraction time in SPME is a key factor in the resulting performance of the method [11]. Fig. 3 includes the extraction time profiles obtained for the zwitterionic PILs together with those of the commercial CAR/PDMS and PA fibers. The extraction time was assessed between 20 and 80 min, followed by thermal desorption for 6 min. Regarding the zwitterionic PIL sorbent coatings, the results indicated that most of the SCFFAs reached equilibrium at around 20 min when using Fiber **1**, while 60 min was required when using Fiber **4**, except for *n*-C_6 and *n*-C_7, which did not reach equilibrium in the time range studied. The peak areas obtained with Fiber **1** at 20 min were similar to those obtained using Fiber **4** with longer extraction times. Therefore, reduced extraction times can be used with Fiber **1** without sacrificing extraction efficiency compared with Fiber **4**. In the case of commercial fibers, most of the smaller SCFFAs reached equilibrium at 60 min using CAR/PDMS, except for *n*-C_4. This analyte, together with *n*-C_6 and *n*-C_7, required more than 80 min to achieve maximum extraction efficiency. For PA, an equilibration time of 40 min was required for all analytes. Therefore, 20 min was selected as the optimum extraction time for Fiber **1**, 40 min for PA, and 60 min for Fiber **4** and CAR/PDMS.

3.3.4. Effect of desorption time

The desorption time was optimized to guarantee quantitative desorption of the analytes from the fibers and avoid *carry over*. The desorption time was studied between 2 and 10 min for both the zwitterionic PIL-based and commercial fibers at their maximum working temperatures. Fig. S4 of the SM includes the time profiles obtained for each fiber. For Fiber **1**, the maximum extraction efficiency for all SCFFAs was obtained after 4 min of desorption, while Fiber **4** provided the best results after only 2 min. For CAR/PDMS, 2 min was sufficient to obtain the highest results for all analytes, except for *n*-C_7. In the case of PA, different behavior was observed depending on the analyte. Better results were obtained with a desorption time of 2 min for *n*-C_4 and *i*-C_6, 6 min for *n*-C_7 and 4 min for the remaining analytes. A desorption time of 4 min was selected as optimum for PA as well as for Fiber **1** whereas 2 min was selected for the remaining fibers.

3.3.5. Effect of ethanol content

The presence of ethanol in the sample can be detrimental for fibers such as CAR/PDMS that extract primarily via an adsorption-type mechanism. However, it should be less important for the developed zwitterionic PILs as they extract via a non-competitive pathway. In addition, carbowax coated fibers can swell in the presence of high organic solvent content. To reinforce this hypothesis, relative recovery (RR) studies were performed under optimum conditions from ultrapure water samples with 1.3% (v/v) ethanol and without ethanol. This ethanol content was selected to mimic the conditions employed when diluted wine samples are analyzed. For estimation of the RR, external calibrations were performed in ultrapure water, as shown in Tables S3–S5 of the SM. If the obtained external calibrations are compared, the results indicated that CAR/PDMS exhibited higher sensitivity for most of the analytes. The exceptions are *i*-C_4 and *i*-C_5 for which similar sensitivities were achieved using all fibers. Furthermore, the zwitterionic PIL fibers provided wider linear ranges for the longer alkyl chain SCFFAs, while the precision of the method (evaluated as the relative standard deviation, RSD) was adequate for all fibers at two different spiked levels.

The RR was calculated as the ratio of the predicted concentration obtained using the calibration curves in ultrapure water (Tables S3–S5) and the spiked concentration; values ranged between 544 and 929 $\mu g\ L^{-1}$ depending on the analyte. The obtained results are shown in Fig. S5 of the SM. The amount of analyte extracted using Fiber **1** was not affected by the presence of ethanol in the aqueous sample, as the same RR values were obtained in both cases for all the SCFFAs. In the case of Fiber **4**, there was a 10–15% decrease in the *i*-C_6 and *n*-C_6 RR values when ethanol was added to the sample, likely due to the higher H-bond basicity of the carboxylate anions of the PIL in comparison with the sulfonate anions of Fiber **1** [8], what could promote certain degree of competence between these analytes and the ethanol. However, similar results were obtained with Fiber **4** for smaller SCFFAs. As expected, the RR values using CAR/PDMS in the presence of ethanol were lower than in ultrapure water. This decrease is sharper for *iso*- and longer alkyl chain SCFFAs, especially in the case of *i*-C_4 and *i*-C_5, for which the RR dropped from 93% to 4.2% and from 110% to 23%, respectively. These results are in accordance with previously observed behavior and suggest that the zwitterionic PIL fibers may be less affected by the presence of ethanol in the sample compared with the CAR/PDMS fiber.

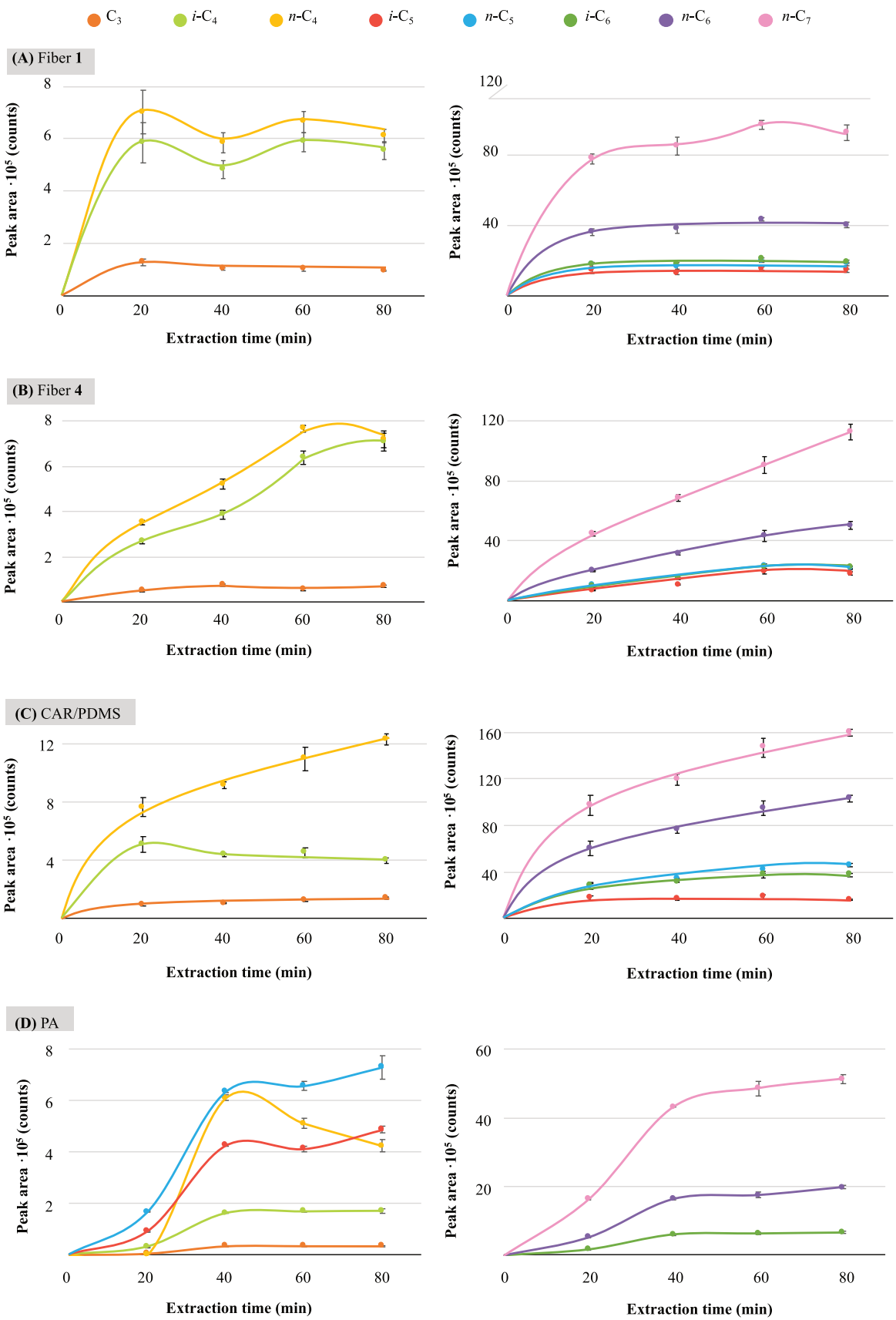

Fig. 3. Extraction time profiles of HS-SPME-GC-MS for the determination of SCFFAs using **(A)** Fiber **1**, **(B)** Fiber **4**, **(C)** CAR/PDMS, and **(D)** PA. Experimental conditions (n = 3): 10 mL of aqueous solution containing the SCFFAs at 0.02 mmol L^{-1}; 30% (w/v) of NaCl; 20–80 min of extraction at 65 °C and 600 rpm; desorption for 6 min at 175 °C for Fibers **1** and **4**, 280 °C for PA, and 290 °C for CAR/PDMS.

Table 3
Analytical figures of merit of the HS-SPME-GC-MS method after performing matrix-matched calibration of diluted synthetic wine.

SCFFA	(Slope ± SD[a])·10^{-4}				LOD[b] (μg·L^{-1})				%RR[c] (%RSD[d])			
	Fiber 1	Fiber 4	CAR/PDMS	PA	Fiber 1	Fiber 4	CAR/PDMS	PA	Fiber 1	Fiber 4	CAR/PDMS	PA
C_3	1.3 ± 0.1	1.4 ± 0.1	1.8 ± 0.1	0.44 ± 0.01	53	36	33	61	115 (1.9)	115 (2.6)	104 (8.4)	88.4 (14)
i-C_4	3.0 ± 0.1	5.3 ± 0.2	7 ± 1	1.7 ± 0.1	60	20	155	57	107 (3.5)	118 (3.8)	120 (5.2)	102 (10)
n-C_4	4.7 ± 0.2	7.2 ± 0.1	24 ± 2	2.1 ± 0.1	40	42	45	47	115 (5.0)	115 (10)	82.7 (6.8)	78.3 (7.5)
i-C_5	4.9 ± 0.2	11.4 ± 0.3	74 ± 10	3.0 ± 0.1	19	26	38	42	112 (4.9)	116 (3.1)	81.5 (6.2)	80.5 (15)
n-C_5	7.0 ± 0.3	14.7 ± 0.3	136 ± 10	4.4 ± 0.1	15	31	8.9	47	105 (4.7)	96.3 (3.5)	98.4 (10)	74.6 (12)
i-C_6	4.3 ± 0.1	11.8 ± 0.4	103 ± 8	2.5 ± 0.1	76	48	10	52	107 (8.6)	107 (3.2)	91.0 (8.1)	115 (5.0)
n-C_6	9.7 ± 0.3	26.3 ± 0.7	202 ± 16	7.1 ± 0.2	22	23	8.4	43	103 (6.2)	98.5 (9.0)	115 (11)	71.2 (13)
n-C_7	17.1 ± 0.4	48.2 ± 0.6	161 ± 9	11.4 ± 0.4	22	12	11	27	93.4 (3.9)	106 (5.5)	112 (11)	95.1 (13)

[a] Standard deviation of the slope.
[b] Limit of detection, calculated as the concentration corresponding to 3 times the signal-to-noise ratio.
[c] Relative recovery for a spiked level of 0.007 mM.
[d] Reproducibility (n = 3) for a spiked level of 0.007 mM.

3.4. Analytical performance of the method

Matrix-matched calibrations in diluted synthetic wine were developed for Fibers **1** and **4**. For comparison purposes, matrix-matched calibrations of CAR/PDMS (adsorption) and PA (absorption) were also included. Table 3 lists analytical figures of merit of the curves, whereas detailed information of the analytical performance for all fibers is included in Tables S6–S9 of the SM.

The calibrations presented wide linear ranges, ranging from 75 to 13300 μg L^{-1} depending on the analyte and fiber. It is interesting to mention that, in general, wider linear ranges were obtained for the absorptive-type fibers (Fiber **1**, Fiber **4** and PA) in comparison to CAR/PDMS.

The sensitivity of the method was evaluated using calibration slopes (Table 3) that ranged from (1.3 ± 0.1)·10^{-4} to (17.1 ± 0.4)·10^{-4} for Fiber **1**, (1.4 ± 0.1)·10^{-4} to (48.2 ± 0.6)·10^{-4} for Fiber **4**, (1.8 ± 0.1)·10^{-4} to (161 ± 9)·10^{-4} for CAR/PDMS, and (0.44 ± 0.01)·10^{-4} to (11.4 ± 0.4)·10^{-4} for PA. The sensitivity of the method was the lowest and highest for C_3 and *n*-C_7 for all fibers, respectively. In general, higher sensitivities were achieved using CAR/PDMS, with the exception of *i*-C_4 for which similar sensitivities were obtained with the zwitterionic PILs. These results are in accordance with the data obtained in Section 3.3.5 indicating the presence of ethanol significantly decreased the extraction efficiency of CAR/PDMS for the extraction of *i*-C_4 with respect to the remaining SCFFAs. The results also indicate that there are other components of the matrix aside from ethanol (i.e., presence of (+)-tartaric acid) that were able to affect the partitioning of analytes to the headspace, likely due to an increase in solubility of the analytes in the initial aqueous sample, among other reasons. In any case, the results demonstrate the suitability of the zwitterionic PILs for this application. If the film thickness of the sorbent coatings is considered, the zwitterionic PILs are significantly thinner than the commercial fibers (18 ± 3 μm for Fiber **1** and 18 ± 6 μm for Fiber **4** versus 75 μm of CAR/PDMS and 85 μm of PA). Improvements to the zwitterionic PIL coating process will produce sorbent coatings as thick as commercial fibers, which should significantly increase the sensitivity of the zwitterionic PILs. As an estimation, Fig. S6 of the SM shows the normalized slopes obtained by dividing the matrix-matched calibration slopes by the film thickness. Normalized slopes 1–3 times higher were achieved for the smaller SCFFAs (C_3–*n*-C_4) and *n*-C_7 if the results of zwitterionic PILs are compared with respect to CAR/PDMS. However, it is important to emphasize that this normalization is an approximation of the sensitivity of the method, independent of film thickness. As the CAR/PDMS fiber extracts via an adsorptive-type mechanism, the analytes interact primarily with the surface of the sorbent coating instead of partitioning into the entire film and, therefore, the sensitivity of this fiber depends on other factors such as the surface area and porosity of the material, among others [11,13].

The limits of detection (LOD) were estimated as the concentration corresponding to three times the signal-to-noise ratio (Table 3). The obtained values ranged between 15 and 76 μg L^{-1} for Fiber **1**, 12–48 μg L^{-1} for Fiber **4**, 8.9–155 μg L^{-1} for CAR/PDMS, and 27–61 μg L^{-1} for PA. These values are particularly low for the determination of SCFFAs [28,29], and are affected by the nature and film thickness of the SPME coating, as described before.

The reproducibility (as RSD) of the method was evaluated at a spiked level of 0.007 mM. The RSD values ranged from 1.9% to 8.6% for Fiber **1**, 2.6–10% for Fiber **4**, 5.2–11% for CAR/PDMS, and 5.0–15% for PA. The RR was calculated at the same spiked level as the ratio of the predicted concentration obtained using matrix-matched calibrations of Table 3 and the spiked concentration. The RR values were acceptable for all fibers.

3.5. Analysis of real samples and study of the matrix effect

The proposed method was applied for the analysis of red wine. Standard addition curves were developed with Fiber **1**, Fiber **4** and CAR/PDMS. PA was excluded in this comparison due to reproducibility problems in the red wine sample, likely from complexity of the sample and its lower sensitivity for the determination of SCFFAs. Tables S10–S12 of the SM show the analytical figures obtained using the standard addition method. The calibration slopes ranged from (0.75 ± 0.03)·10^{-4} to (83 ± 2)·10^{-4} for Fiber **1**, (1.6 ± 0.1)·10^{-4} to (74 ± 3)·10^{-4} for Fiber **4**, and (2.1 ± 0.1)·10^{-4} to (315 ± 10)·10^{-4} for CAR/PDMS.

A study of red wine matrix effects was performed by a statistical comparison of the calibration slopes obtained in matrix-matched calibrations (Table 3) and the standard addition method. The comparison method was performed using the Student's *t*-test considering the standard deviation of the residuals at a 95% confidential level [40]. The results indicated a significant matrix effect for the majority of analytes/sorbent coatings (see Tables S13–S15 of the SM). Therefore, equal slopes were found only for *i*-C_4 for Fiber **1**; C_3, *i*-C_4 and *n*-C_4 for Fiber **4**; and C_3 and *i*-C_5 for CAR/PDMS. It is interesting to note that, for the rest of the analytes (excluding the cases where the slopes were equal), an enhancement of the sensitivity was observed when the standard addition method was employed and slopes between 1.3 and 4.8, 1.1–1.5 and 1.2–1.9 times higher were obtained using standard addition for Fiber **1**, Fiber **4** and CAR/PDMS, respectively.

Considering the significant matrix effect for the majority of SCFFAs, standard addition was selected for the quantification of the analytes in red wine. Fig. 4 shows the predicted concentrations. The analytes *i*-C_4 and *n*-C_5 were not detected using CAR/PDMS as this fiber was negatively affected by the presence of ethanol. In the remaining cases, no significant differences in the SCFFAs concentrations were observed for

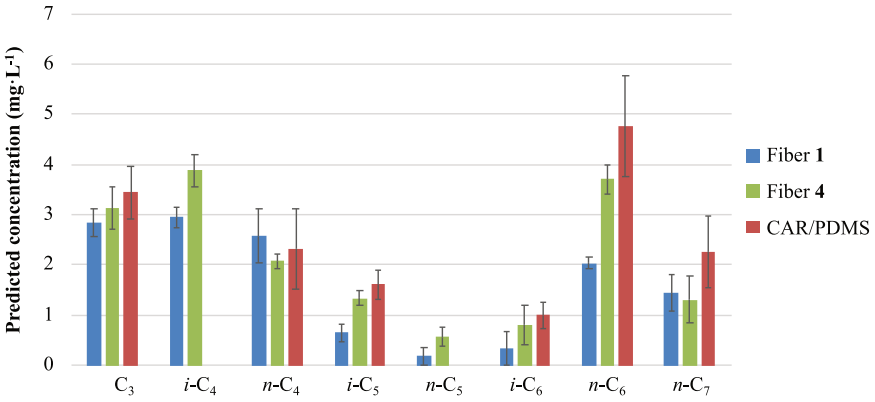

Fig. 4. Analysis of red wine using the standard addition method and different SPME fibers.

Fiber **4** respect to CAR/PDMS, and in the C_3, *i*-C_6 and *n*-C_7 concentrations for Fiber **1** respect to CAR/PDMS. These results demonstrated the potential of these zwitterionic PILs for the analysis of real samples. The SCFFA concentrations ranged from $0.18 \pm 0.03\,mg\,L^{-1}$ to $4.8 \pm 0.9\,mg\,L^{-1}$, depending on the fiber. The presence of SCFFAs in wine is commonly associated with the fruity, fatty and rancid aroma of wines [41].

The proposed method was compared with other methods from the literature that used GC for the determination of SCFFAs. The proposed method provided similar analytical performance to previously reported HS-SPME methods for the determination of SCFFAs in wine [26], while it is simpler than other SPME modes employed for FFA determination such as vacuum HS-SPME [29] and faster than multiple HS-SPME [28].

4. Conclusions

A new type of zwitterionic PIL sorbent coating was developed and successfully applied in HS-SPME for the determination of SCFFAs. The sorbent coatings were generated by the co-polymerization of ZIL monomers based on 1-vinyl-3-(alkylsulfonate)imidazolium or 1-vinyl-3-(alkylcarboxylate)imidazolium and dicationic IL crosslinkers. A preliminary comparison of the different zwitterionic PILs for the extraction of SCFFAs via HS-SPME revealed that the fibers containing the [$VIm^+C_9COO^-$] ZIL monomer provided better results, while the length of the alkyl chain substituent in the 1-vinyl-3-(alkylsulfonate)imidazolium monomers did not influence the extraction efficiency. A study of the primary extraction mechanism of the zwitterionic PILs revealed that the sorbent coatings extracted via a non-competitive mechanism. This study also demonstrated that the nature of PILs can be easily tuned for achieving high selectivity while also promoting absorption/adsorption.

A HS-SPME-GC-MS method was optimized for the best performing zwitterionic PILs (Fiber **1** and Fiber **4**), CAR/PDMS and PA. The results indicated that equilibrium can be reached faster with Fiber **1** while presenting similar extraction efficiency than the remaining fibers for smaller and *iso*- SCFFAs. The zwitterionic PILs were more sensitive than the most suitable absorptive-type fiber (i.e., PA), and less affected by the ethanol content than the most suitable adsorptive-type fiber (i.e., CAR/PDMS). Similar LODs were achieved with the zwitterionic PILs and CAR/PDMS in synthetic wine, but the zwitterionic PILs were more reproducible than the commercial fibers. The zwitterionic PILs were successfully applied for the analysis of red wine using the standard addition method. The obtained results with zwitterionic PILs were in accordance with those obtained with CAR/PDMS. Fibers **1** and **4** detected *i*-C_4 and *i*-C_5, although CAR/PDMS was not able to detect them due to the interference by ethanol. The SCFFA concentrations determined in red wine ranged from $0.18 \pm 0.03\,mg\,L^{-1}$ to $4.8 \pm 0.9\,mg\,L^{-1}$, depending on the analyte and fiber. On-going work is devoted to improving the coating process to obtain thicker sorbent coatings in an effort to increase the sensitivity of the method.

Acknowledgements

IPF acknowledges the Agencia Canaria de Investigación, Innovación y Sociedad de la Información (ACIISI), co-funded by the European Social Fund, for her FPI PhD fellowship. IPF also acknowledges the program Fostering Grads (ECUSA-ULL) and Cabildo de Tenerife for the funding of her short-term stay. JLA acknowledges funding from Chemical Measurement and Imaging Program at the National Science Foundation (Grant number CHE-1709372). KK thanks KAKENHI (18K14281 from the Japan Society for the Promotion of Science) and Leading Initiative for Excellent Young Researchers (from Ministry of Education, Culture, Sports, Science and Technology-Japan). ALH and MBJ acknowledge the Concordia Chemistry Department Research Endowment.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2019.03.073.

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